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Analysis of the Near Ultraviolet Electronic Transition of Benzene

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The absorption spectrum of benzene at 2800–2200A has been analyzed. The vibrational structure of the system has been found to be in agreement with the selection rules for a forbidden transition ($^1A_{1g} \rightarrow {}^1B_{2u}$). The transition becomes possible when vibrations of type E_g^+ distort the molecule. Only carbon frequencies have been found to be effective. The interpreted data are collected in series on page 211. The analysis is corroborated by comparison with the absorption of solid benzene at −259°C, with the absorption spectrum of heavy benzene and with the fluorescence spectra of both benzenes.

INTRODUCTION

THE weak electronic band system observed in benzene in the region from 2200 to 2800A has been the subject of numerous investigations. It has been studied in absorption[1] as well as in fluorescence,[2] the spectra having been obtained in the gaseous and condensed[3] phase.

The first theoretical treatment of the electronic states of benzene has been given by Hückel.[4] Sklar[5] has pointed out that the lowest excited singlet level in all probability corresponds to the upper state of the above-mentioned system. He has shown especially that the spectral position of the bands is in agreement with the thermal data (resonance energy) of some hydrocarbons. The weak intensity of the band system agrees with the assignment to a forbidden transition.

It is known that for diatomic molecules the rotational band structure allows some conclusions on the symmetry of the respective electronic levels. For polyatomic molecules such a rotational analysis cannot in general be carried through, but instead the larger variety of their vibrations yields analogous information regarding the electronic states. In this paper we will investigate which vibrational structure follows from assumed symmetries of the theoretical electronic levels for the transition in question, and we will then compare it with the experimental facts. It will be seen that the complicated structure of the absorption and fluorescence spectra can, to a large extent, be understood on the basis of Sklar's proposals for the symmetry of the excited elec-

[1] R. Witte, Zeits. f. wiss. Phot. **14**, 347 (1915); K. Schulz, Zeits. f. wiss. Phot. **20**, 1 (1920); V. Henri, J. de phys. et rad. (6), **3**, 181 (1922) and *Structure des Molécules* (Hermann, Paris, 1925), p. 108 ff.; G. B. Kistiakowsky and A. K. Solomon, J. Chem. Phys. **5**, 609 (1937); A. Ionescu, Comptes rendus Acad. Roum. **2**, 39 (1937).

[2] G. B. Kistiakowsky and A. Nelles, Phys. Rev. **41**, 595 (1932); G. R. Cuthbertson and G. B. Kistiakowsky, J. Chem. Phys. **4**, 9 (1936); C. K. Ingold and co-workers, J. Chem. Soc. p. 912 (1936).

[3] A. Reimann, Ann. d. Physik **80**, 43 (1926); P. Pringsheim and A. Kronenberger, Zeits. f. Physik **40**, 75 (1926); A. Kronenberger, *ibid.* **63**, 494 (1930).

[4] E. Hückel, Zeits. f. Physik **70**, 204 (1931); Zeits. f. Elektrochem. **43**, 752 (1937); L. Pauling and A. Sherman, J. Chem. Phys. **1**, 606, 679 (1933).

[5] A. L. Sklar, J. Chem. Phys. **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. **6**, 645 (1938).

tronic state. In this way we will obtain a justification of his conclusions about the nature of the electronic term.

General Theoretical Discussion

Sklar deduces from symmetry considerations that the electronic transition in question is a forbidden one. Now the vibrational structure of a forbidden transition differs in a characteristic way from that of an allowed one.[6] It is plausible to assume that the symmetry of the equilibrium position is the same in both the ground and excited states. It can then be derived[7] from the Franck-Condon principle that, in the case of an allowed electronic transition, the quantum number of the totally symmetrical vibration will be the principal one to change. In forbidden transitions, however, there must occur a change of a nontotally symmetrical vibration by at least one quantum, upon which changes of the totally symmetrical vibrations might then be superposed. The perturbation of the electronic level caused by this nontotally symmetrical vibration makes the transition, forbidden for itself, appear with weak intensity.

Applying these considerations to the benzene spectrum we should expect long progressions of the totally symmetrical vibrations, if the nuclear distances are slightly different in the upper and lower electronic states. Progressions of the totally symmetrical frequencies of the ground state; namely 992 cm^{-1} (for the change in the C−C distance) and 3062 cm^{-1} (for the change in the C−H distance), should occur mainly in the fluorescence spectrum and progressions with the corresponding frequencies in the upper state, in the absorption spectrum.

In the case of an allowed transition these progressions, involving only the totally symmetrical vibrations, should occur with predominating intensity. We should furthermore find intense 0–0, 1–1, $\cdots$ n–n transitions of all the nontotally symmetrical vibrations, unless they are weakened too much by Boltzmann factors. There should also occur, though with very low intensity, 0–2, 1–3, etc. transitions of nontotally symmetrical vibrations and also some combination frequencies. At low temperatures, i.e. for solid benzene, the absorption spectrum should become exceedingly simple, showing only the 0–n progressions of the totally symmetrical vibrations, weak 0–2 transitions of nontotally symmetrical vibrations and also weak combinations. If in the absorption spectrum of benzene at room temperature bands appear on the long wave-length side of the 0–0 band, they should be associated with a totally symmetrical vibration (except in the cases where they could be interpreted as n–n transitions of any vibration).

This last statement gives a strong argument against the assumption of an allowed electronic transition for the band system under investigation. This band system exhibits in vapor absorption two major progressions of band heads spaced 923 cm^{-1}, going from longer to shorter waves but starting 1126 cm^{-1} apart. The progression beginning at shorter wave-lengths is the stronger one, and in case of an allowed transition its first member should be the 0,0 band. In the absorption of the crystal at −259°K, the stronger progression (for the moment assumed as the 0–0 transition for the gas) is also present. The weaker progression of the vapor, however, is completely absent. On the other hand, a very weak band is found shifted by 550 cm^{-1} toward the red from the first member of the main progression. This makes it impossible to interpret the above mentioned strongest band as the 0,0 band, since at such low temperatures no band may appear on the long wave side of the 0,0 band. In the case of a forbidden transition, however, no strong 0,0 band should be visible, and the strongest observed band will be due to the 0–1 transition of one of the nontotally symmetrical vibrations of the proper symmetry. To determine the nature of such vibrations we must first discuss the symmetries of the electronic states.

The ground state of the benzene molecule is one of total symmetry ($^1A_{1g}$ Tisza-Placzek-Mulliken notation, $^1\Gamma_1$ Bethe-Wigner notation).[8] The

[6] These differences refer to selection rules which are not concerned with changes in multiplicity.

[7] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

[8] Here A and B mean nondegenerate levels symmetrical (s) and antisymmetrical (a) with respect to a rotation by 180° about the sixfold axis (or z axis). The subscripts 1,2 and g,u imply s or a to rotation about a twofold axis through nuclei and to an inversion through the center, respectively. Doubly degenerate states are designated by E. Their s and a character with respect to a rotation by π

only excited electronic level consistent with Sklar's theoretical derivations and the foregoing is a nondegenerate one which is antisymmetric with respect to rotations by 60° about an axis perpendicular to the plane of the molecule (z axis), to a rotation about a twofold axis through nuclei and to an inversion through the center ($^1B_{2u}$ or $^1\Gamma_{10}$). The z component of the electric moment (vertical to the plane of the ring) for the transition between these two levels transforms like $\Gamma_1\Gamma_8\Gamma_{10}=\Gamma_3$ or $A_{1g}A_{2u}B_{2u}=B_{1g}$, while the horizontal component transforms like $\Gamma_1\Gamma_{12}\Gamma_{10}=\Gamma_5$ or $A_{1g}E_u{}^-B_{2u}=E_g{}^+$. According to this the 0,0 band is forbidden, and group theoretical considerations show that the electronic transitions can only be made allowed (although of weaker intensity than a normally allowed transition would be) when vibrations of symmetry character $\Gamma_3(B_{1g})$ or $\Gamma_5(E_g{}^+)$ are excited either in the ground state or in the excited state or in both. Wilson's[9] discussion of the possible types of vibrations of the benzene molecule shows that there are no vibrations of symmetry $\Gamma_3(B_{1g})$. Hence we expect in the spectrum only the excitation of the twofold degenerate vibrations of symmetry Γ_5 or $E_g{}^+$ or simultaneous excitation of several like or different frequencies, provided their direct product contains Γ_3 or Γ_5 (the combination vibrations, however, appearing with much weaker intensities). As pointed out in the foregoing we must take, instead of a 0,0 band, one of the $E_g{}^+$ vibrations occurring in 0–1 or 1–0 transitions as first members of the progressions with 923 cm^{-1} spacing. Benzene possesses four $E_g{}^+$ vibrations in the ground state and corresponding ones in the excited state. The values in the ground state are known from Raman measurements: 606.4, 1178, 1596 and 3047 cm^{-1}. We cannot decide from symmetry considerations alone which of these will occur and with which intensity.[10] It can be said that a C vibration will be a more effective perturbation than an H vibration, since the transition is between two states of the π electrons which affect only the C–C bonds. We expect, accordingly, that only the C vibrations will be important in producing this transition. This is in agreement with the known fact that a substitution of the hydrogen atoms by halogens, for example, does not affect appreciably the appearance nor the strength of absorption. Of the mentioned $E_g{}^+$ frequencies, the 606.4 and 1596 cm^{-1} are known to be C vibrations. According to Kistiakowsky and Solomon[11] the 606.4 frequency drops to 526 cm^{-1} in the upper level. Our analysis confirms this with but a slight change of the value to 520 cm^{-1}. The 0–1 and 1–0 transitions of this vibration differ by $606.4+520=1126.4$ cm^{-1} which is the distance between the two major progressions. The corresponding transitions involving the 1596 frequency are also present as we shall see later. The difference of 1126.4 cm^{-1} is also observed in high pressure fluorescence. In solid benzene at -259°C we can expect only the 0–1 transition, since the 1–0 cannot appear on account of the Boltzmann factor. However, we may expect the 0,0 band weakly in solid benzene in violation of the selection rules, since it becomes possible here through the action of crystal forces.

These conclusions are in complete agreement with observations in heavy benzene,[12] which show unambiguously that the 0–1 and 1–0 transitions, which make the electronic jump allowed, involve C vibrations because of their close similarity to the corresponding vibrations in light benzene.

Absorption Spectrum of Gaseous Benzene

1. Vibrational analysis

A small reproduction of the absorption spectrum[13] of gaseous benzene is given in Fig. 1. From such spectrograms taken by Radle and Beck a schematic representation has been made for those bands which we have been able to interpret (Fig. 2). The diagram is only roughly to scale, especially with respect to the relative intensities.

about the sixfold axis is designated by the superscript + or −.

[9] E. B. Wilson, Phys. Rev. **45**, 706 (1934).

[10] The interpretation presented in a preliminary report (Phys. Rev. **53**, 932 (A) (1938)) had to be changed to some extent.

[11] G. B. Kistiakowsky and A. K. Solomon, J. Chem. Phys. **5**, 609 (1937). The discrepancy of the 6 cm^{-1} will be explained later.

[12] New data on heavy benzene have been obtained by one of the authors (H. Sp.) and will be published soon.

[13] We are very much obliged to Mr. Radle and Dr. Beck of the Catholic University of America for letting us use their spectrograms and their wave-length measurements before their own publication, and we wish to express our sincere thanks for their helpfulness.

FIG. 1. Absorption spectrum of benzene.

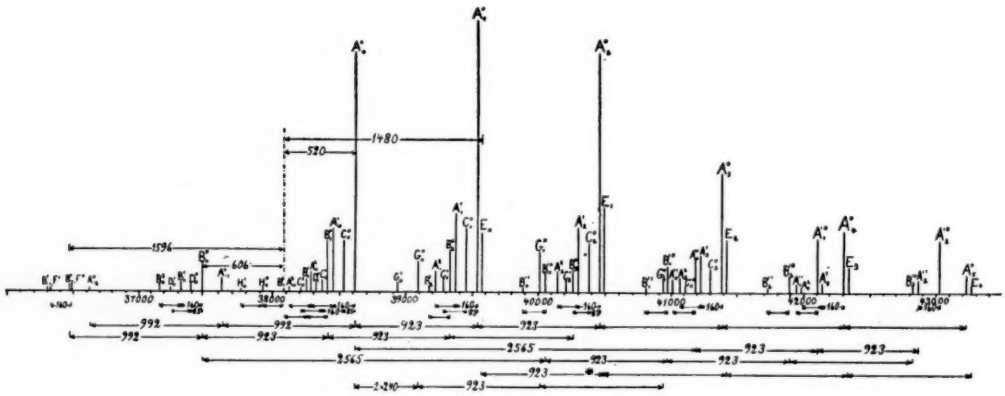


FIG. 2. Schematic absorption spectrum of benzene.

The different band series are denoted[14] with capital letters where the subscripts refer to the change in quantum numbers of the totally symmetrical C vibration of 992 cm^{-1} in the ground state (negative subscripts) and of 923 cm^{-1} in the upper state (positive subscripts). The primes designate bands starting 2565 cm^{-1} (totally symmetrical H vibration in the excited state) from the main bands. The superscripts refer to the frequency *differences*[15] of 160 cm^{-1} which appear on the long wave-length side of each member of the main progressions.

A considerable number of the bands apparently show structure. It looks as if some of the stronger bands, e.g. C_0^0 (38,524/31) had double heads. As discussed in the next section, we ascribe the heads to rotational[16] structure, i.e. we interpret them as R and Q branches, the R branch usually being the weaker one on the short wave-length side, since the bands are degraded towards the red. We find about 6 cm^{-1} for the distance between the two heads. In the strongest bands, e.g. A_0^0, the absorption is so intense that the structure is no more discernible, and the edge presumably corresponds to the R head. Thus, in order to be consistent we have to measure frequency differences between the strong Q-branches and accordingly subtract 6 cm^{-1} from the measured edges of the strongest bands. Therefore, for example, we obtain for the Q branch of the band A_0^0 the frequency 38,608.7 cm^{-1} instead of the measured value of the edge 38,614.7 cm^{-1}.

The position of the theoretical 0,0 band can now be determined. As we have already pointed out in the previous section, the difference of 1126.4 cm^{-1} between the first members of the two strongest progressions[17] at 37,482.3 cm^{-1} and 38,608.7 cm^{-1} can be divided into the two known frequencies $606.4+520=1126.4$ cm^{-1}. Since the frequency 606.4 cm^{-1} belongs to the ground state and 520 cm^{-1} to the excited one, our 0,0 band would be $37,482.3+606.4=38,609.7$

[14] We have tried, as much as possible, to follow the notations of Ingold and co-workers (reference 2).

[15] Progressions with the spacing of 160 cm^{-1} will be discussed later.

[16] It should be pointed out that our interpretation of the rotational structure is a tentative one, and if it should later be found that the double heads are independent bands, our argument for subtracting 6 cm^{-1} from the frequencies of the strongest bands would no longer be valid.

[17] The value of 37,482.3 cm^{-1} denotes the Q branch; at higher pressures a weak second band head appears 6 cm^{-1} to the short wave-length side of it.

$-520=38{,}088.7$ cm^{-1}. This interpretation is borne out in heavy benzene.

With the calculated value of the 0,0 band, the interpretations which we have given to the different series are listed in the following equations:[18]

A series:

$$\nu=38{,}089+520+v_1'\times 923-v_1''\times 992+v_2\times 2565-v_3\times\underbrace{(400-240)}_{160}. \quad (1)$$

B series:

$$\nu=38{,}089-606.4+v_1'\times 923-v_1''\times 992+v_2\times 2565-v_3\times 160. \quad (2)$$

C series:

$$\nu=38{,}089+2\times 520-606.4+v_1'\times 923+v_2\times 2565-v_3\times 160. \quad (3)$$

D series:

$$\nu=38{,}089+520-2\times 606.4+v_1'\times 923-v_3\times 160. \quad (4)$$

E series:

$$\nu=38{,}089+1480+v_1'\times 923. \quad (5)$$

F series:

$$\nu=38{,}089-1596-v_3\times 160. \quad (6)$$

G series:

$$\nu=38{,}089+520+2\times 240+v_1'\times 923-v_3\times 160. \quad (7)$$

H series:

$$\nu=38{,}089-v_3\times 160. \quad (8)$$

where $v_1'=0,1\cdots$; $v_1''=0,1,2$; $v_2=0,1$; $v_3=0,1\cdots$.

The first member of the *A* series, A_0^0, which is the band at 38,608.7 cm^{-1}, appears in our interpretation as the 0–1 transition of one of the $E_g^+(\Gamma_5)$ *C* frequencies (520 cm^{-1} in the upper state) and correspondingly the first member of the *B* series, B_0^0, (37,482.3) is the 1–0 transition of the same frequency (606.4 cm^{-1} in the ground state). This confirms the prediction that the Γ_5 *C* frequencies would give the most intense bands in the system, since only a Γ_5 vibration is allowed as a 0–1 or 1–0 transition. The 1–0 transition is expected to be weaker by a computed Boltzmann factor of 17 which agrees with the spectrogram.[19]

The above 0–1 transition starts a progression of six members with 923 cm^{-1} spacing to shorter wave-lengths; 923 cm^{-1} is thus the totally symmetrical vibration in the excited state. The second member, A_1^0, $(0\rightarrow 520+923)$ is[20] apparently slightly more intense than the first band $A_0^0(0\rightarrow 520)$ and third band A_2^0 $(0\rightarrow 520+2\times 923)$ which seem to be of equal intensity. This fact allows some conclusions concerning the increase in internuclear distance in the excited state (cf. next section).

The totally symmetrical *H* vibration may also occur superimposed on the allowed transition. Since the electronic excitation will probably not change the C–H distance, and also since the frequency is large, it is likely that not more than one member will appear. Now, a band distant by about 2565 cm^{-1} from the A_0^0 band (38,608.7) is found at 41,171 cm^{-1}, (A_0'), and there are also observed two bands spaced 923, (A_1'), and 2×923 cm^{-1}, (A_2'), from the first one. All three bands appear strikingly in the crystal. We accordingly interpret the frequency difference 2565 cm^{-1} as the totally symmetrical *H* vibration in the excited state (3062 cm^{-1} in the ground state).

[18] In order to facilitate the comparison with previous representations of the series, we mention that some of the equations correspond to the following ones quoted from the paper of Kistiakowsky and Solomon (reference 11).

A series to 1:
$1/\lambda=38{,}624+921.4n-161p$; $n=0,1\cdots$; $p=0,1\cdots$.
B series to 2:
$1/\lambda=37{,}494+921.4n-161p$; $n=0,1\cdots$; $p=0,1\cdots$.
C series to 3:
$1/\lambda=38{,}537+921.4n-161p$; $n=0,1\cdots$; $p=0,1\cdots$.
D series to 4:
$1/\lambda=37{,}426+921.4n-166p$; $n=0,1\cdots$; $p=0,1\cdots$.
E series to 5:
$1/\lambda=38{,}656+920n-162p$; $n=0,1\cdots$; $p=0,1\cdots$.

There appears, however, no band corresponding to the first member of the series 5 and also no 160 progression can be seen. Series 6 in the quoted paper

6. $1/\lambda=39{,}649+920n$; $n=0,1\cdots$

could also be traced starting with the band 39,638 cm^{-1} (though not in the spectrum of heavy benzene), but no unambiguous interpretation can be given. Progressions of 120 cm^{-1} spacing have occasionally been reported, but we find them spurious. The first member of our *A* series, A_0^0, is 38,608.7 cm^{-1}, while Kistiakowsky and Solomon quote it as 38,624 cm^{-1}. To explain this discrepancy we note first that in our interpretation we have to subtract 6 cm^{-1}, which gives 38,618 cm^{-1}. Furthermore, part of the deviation is due to the fact that our wave numbers have been reduced to vacuum, while those in Henri's older paper (1922) from which these equations have been taken are not. This gives a correction of 11 cm^{-1}. The remaining 2 cm^{-1} must be ascribed to the greater accuracy of Beck and Radle's measurements.

[19] The intensity ratio of these two bands was visually estimated and is now being measured by Radle and Beck (cf. reference 13).

[20] The arrows indicate the direction of absorption.

The totally symmetrical C vibration of 992 cm^{-1} in the ground state is found superimposed on the allowed 0–1 transition in the band 37,618 cm^{-1} (A_{-1}^0). Its weak intensity is in accord with the theoretical Boltzmann factor of 1/100. With a very large absorption path, Radle has found a band at 36,637.9 (A_{-2}^0) which corresponds to a second displacement by 992 cm^{-1} (the Boltzmann factor is 10^{-4}).

The same progressions as discussed above occur in conjunction with the B series, the first member, B_0^0, being the band 37,482.3 cm^{-1}, corresponding to the transition from 606.4 cm^{-1} in the ground state to the vibrationless upper state. We find three bands spaced 923 cm^{-1} to shorter wave-lengths and one spaced 2565 cm^{-1} at 40,050 cm^{-1} (B_0'), which in turn is repeated three times with 923 cm^{-1} spacing. A band shifted by 992 cm^{-1} towards longer wave-lengths from the band B_0^0 is observed through a very long absorption path with the expected very low intensity. It appears as a doublet (bands at 36,478 and 36,497 cm^{-1}) just as in the Raman spectrum. The explanation is the same for both spectra; namely, the accidental degeneracy of the 1596 (Γ_5) frequency with 606.4+992 cm^{-1}. Therefore one of the degenerate levels corresponds to our F band (the 1–0 transitions of the larger Γ_5 C frequency) and both appear with extremely low intensity because of the Boltzmann factor.

We believe the 0–1 transition containing the larger E_g^+ C frequency in the upper state to be also present. The band assigned to this transition is 39,569, which gives 1480 cm^{-1} for the value of the Γ_5 C frequency (1596 cm^{-1} in the ground state). Superimposed on this band we find three members of the 923 cm^{-1} progression. This group of bands is comprised in the E series.

There exist two other prominent band series in the absorption spectrum of the vapor, denoted here by C and D. The first member of the C series, C_0^0 (38,524 cm^{-1}) has a distance of 85 cm^{-1} from A_0^0 (38,608.7 cm^{-1}), which was interpreted as the transition 0→520. As already proposed by Kistiakowsky and Solomon[11] in connection with their measurements of the temperature coefficient (to be discussed later) the former transition starts from the 606.4 cm^{-1} vibration in the ground state. We interpret the C series as the transition 606→2×520 (1–2 transition of the Γ_5 C vibration). Likewise the band D_0^0 at 37,394 cm^{-1} (displaced by 88 cm^{-1} from the B_0^0 band at 37,482 cm^{-1}) can be assigned to the transition 2×606→520 (2–1 transition of the Γ_5 vibration). Progressions with 923 cm^{-1} spacing are superimposed on both the C_0^0 and D_0^0 bands, and in addition we find a weak band $C_0'^0$ distant by 2565 cm^{-1} from C_0^0.

On the longer wave-length side of the bands A_i^0, B_i^0, C_i^0, D_i^0 (where $i=0,1\cdots$ and denotes the different members of the 923 cm^{-1} progressions), there appear other bands distant 160 cm^{-1} (denoted A_i^1, B_i^1, C_i^1, D_i^1) or multiples of this quantity. The origin of these progressions has been the subject of much discussion. On the basis of measurements of the temperature dependence of the intensity, Kistiakowsky and Solomon have attributed the 160 cm^{-1} progressions to a series of transitions from the ground state with n quanta of a low vibration to the excited state with n quanta of the same vibration which has dropped by 160 cm^{-1}. They propose the 400 cm^{-1} frequency, known from Raman effect, which would drop to 240 cm^{-1}, as best fitting to their data. This assignment of the 160 cm^{-1} is also indicated by calculations on the heat capacity and entropy of benzene[21] which are critically sensitive to very low normal vibrations. The interpretation of the 160 cm^{-1} progressions as due to a series of n–n transitions of a low frequency is in accord with our views. From the spectrum alone one cannot decide to which vibrational symmetry this frequency has to be ascribed. It is clear, however, that the 160 cm^{-1} spacing must be associated with a carbon vibration, both because the frequency is small (from temperature measurements) and because in heavy benzene the 160 frequency difference drops only to 140 cm^{-1}. Also as the frequency is low, it must correspond to a bending vibration; this limits us to a choice between the $\Gamma_{11}(E_u^+)$ and $\Gamma_4(B_{2g})$. Now the 400 cm^{-1} frequency is identified with the E_u^+ vibration, since a Raman frequency of 373 cm^{-1} has been found in 1, 3, 5 trideuterobenzene.[22] The reduced symmetry of

[21] R. C. Lord and D. H. Andrews, J. Chem. Phys. **41**, 149 (1937).

[22] A. Langseth and R. C. Lord, Danske Vidensk. Selskab. Math. Fys. Meddelelser. **16**, 6 (1938); C. K. Ingold, Proc. Roy. Soc. **A169**, 149 (1938).

a symmetrical trisubstituted benzene is such that an E_u^+ vibration becomes allowed in the Raman effect while the B_{2g} remains forbidden.

That one should associate the 160 cm^{-1} frequency difference with the 400 cm^{-1} E_u^+ vibration is supported by the appearance of a band, both in the vapor and in the crystalline absorption at $-259°C$, which fits the assignment $(G_0^0)0 \rightarrow 520 + 2 \times 240$, the 240 being $400 - 160$. It is, however, at first surprising that a low frequency should drop so much in the excited state, i.e. by 40 percent. An abnormal drop, on the other hand, is expected for just such a low frequency whose restoring force is due to the π electrons, in view of the fact that the excitation energy weakens this restoring force. In fact, a rough estimate for the drop can be made as follows. If one excites this frequency with a sufficiently great amplitude (e.g. 1 or 1.5A), then the energy difference between the excited electronic state and the ground state approaches zero, since the exchange energy of π electrons is large only for the plane structure. This gives the change in restoring force which together with the frequency in the ground state then yields an estimate for the frequency in the excited state. One thus finds that the frequency 400 cm^{-1} drops to a value between 230 and 330 cm^{-1}.

Although our new analysis accounts for most of the strong bands of the absorption spectrum, it contradicts conclusions of Kistiakowsky and Solomon concerning the origin of the B series. Their investigations of the temperature dependence of the intensity of the bands A_0^0 and B_0^0 (first members of the two major progressions, respectively) showed that in the range from 32°C to 220°C the levels from which both bands originated were continually depopulated with increasing temperature. They interpreted this fact as evidence that the transitions involved arose from the vibrationless ground level. The band B_0^0 would then have to be regarded as the 0,0 band and A_0^0 as due to a $0 \rightarrow 1132$ transition.[23]

[23] One objection (already foreseen by Kistiakowsky and Cuthbertson, referente 2) would be that the value 1132 presumably designates the $\Gamma_6 H$ vibration in the excited state which is 1178 cm^{-1} in the ground state. As an H vibration this value drops considerably in heavy benzene (to 878). Now in heavy benzene the separation of the two major bands is 1076, i.e., only 56 cm^{-1} less than in light benzene.

We too assigned the band A_0^0 to a transition from the vibrationless ground state $(0 \rightarrow 520)$. However, we found it necessary to interpret the band B_0^0 as a transition from a vibrating lower level $(606 \rightarrow 0)$. This assignment is not in direct contradiction to the temperature data, since a depopulation with increasing temperature (in a range far above 0°K) does not necessarily imply a vibrationless level. In other words, at elevated temperatures not only the ground level but also the lower vibrational states can be depopulated with rising temperatures, if there are many vibrations close above them. This is the case in benzene, where the *a priori* probability for a higher excitation increases strongly due to the many possible combinations of its thirty vibrations. A statistical calculation shows that the present data for temperature coefficients is in about as good agreement with the Boltzmann factor of the 606.4 cm^{-1} vibration as with the vibrationless state, while they seem to agree best with the Boltzmann factor of a 400 cm^{-1} vibration. The difficulty of measuring the successive decreases in intensity probably precludes sufficient accuracy to decide exactly which level is responsible, but a decision on this point could be reached in the following way. At sufficiently low temperatures the population of every vibrational level is decreased, whereas the population of the ground state is, of course, greater than at higher temperatures. Measurements on B_0^0 at $-15°C$ have shown such a decrease in intensity, although a danger of nonequilibrium in the experiments has detracted from conclusiveness. It would hence be highly desirable to repeat the measurements at this temperature.

The whole discussion so far referred to the strong bands in the spectrum. Besides these we should expect many weaker bands. First, 0–2, 1–3$\cdots$ transitions or even changes of quantum numbers of any vibration may be superimposed on already allowed transitions. The intensity of bands belonging to transitions which involve large changes in quantum numbers of nontotally symmetrical vibrations will be very low. In fact, for an allowed transition, or one made allowed by some interacting vibration V_1, the following intensity ratio[7] holds for the changes in the quanta of any second nontotally symmetrical vibration V_2.

$$\tau=\frac{(\nu'\nu'')^{\frac{1}{2}}}{\frac{1}{2}(\nu'+\nu'')}=\frac{\text{intensity of band } 0-0 \text{ in } V_2}{\text{intensity of all bands } 0-n \text{ in } V_2};$$

$$n=0, 2, 4\cdots,$$

where ν' and ν'' are the frequencies in the two electronic states of V_2. We should expect 0–2 transitions to be most easily observed.[24] Besides a 0–2, 1–3$\cdots$ transition any other transition may occur as long as the additional excitation of vibrations does not change the symmetry of the vibrational eigenfunction. In addition, transitions involving any combination of quanta of the same or different vibrations may appear directly superimposed on the 0,0 transition if the direct product of the vibrational eigenfunctions in the initial and final states contains E_g^+ or B_{1g} (Γ_5 or Γ_3). Intensities of such transitions would be lower by about the same factor as the intensity ratio between the first overtone and the fundamental in the Raman effect; namely about 1/100.

Owing to the many possible combinations of partly unknown frequencies, we have found it extremely difficult to give unambiguous interpretations for the weaker bands, and we therefore prefer to restrict ourselves to the discussion of two band series which involve independently evaluated upper frequencies and which seem to be reasonably certain. They are contained in our *G* and *H* series, the first members being the bands at 39,087 and 37,929 cm^{-1}, respectively. The *G* series, which appears in the spectrum of the gas and the solid, is an example of a 0–2 transition superimposed on an allowed transition. The *H* series, on the other hand, is made allowed by the excitation of an E_u^+ vibration in both the ground and excited states. It consists of two weak bands displaced by 160 and 2×160 cm^{-1} from the 0,0 band. Since the 0,0 band coincides with the band B_1^2, H^0 and H^1 could also be identified as B_1^3 and B_1^4. However, by comparison with the intensity of the 160 cm^{-1} progression, superimposed on A_0^0, which should certainly be much stronger, we conclude that the members B_1^3 and B_1^4 would be far too weak to be observed and hence the bands are to be interpreted as members of a new series H^0 and H^1 directly superposed on the 0,0 transition. Confirmation of both series will be reported in the analysis of the heavy benzene spectrum.

The analysis which has been proposed in this section receives strong support from a consideration of the corresponding spectrum in heavy benzene. In fact, a considerable part of the interpretation was obtained through the comparison with heavy benzene. The frequency difference between the two major progressions which is 38,608.7 − 37,482.3 = 1126.4 in light benzene is 38,789 − 37,713 = 1076 cm^{-1} in heavy benzene.[25] As is known from Raman effect measurements, the E_g^+ 606 cm^{-1} frequency drops to 579 cm^{-1} in C_6D_6, leaving 497 cm^{-1} for its value in the excited state (compared to 520 cm^{-1} in C_6H_6). An independent check for the value of 520 cm^{-1} was furnished by the measured frequency difference, in C_6H_6, of 86 cm^{-1} = 606 − 520 between the first members of the main progressions *A* and *C* and also by that between *B* and *D*. The corresponding bands in heavy benzene are separated by 82 cm^{-1} = 579 − 497.

The spectrum of heavy benzene gives additional confirmation also in the following point. In the spectrum of C_6H_6 a doublet was found (see the bands 36,497 and 36,478 cm^{-1}) corresponding to the Fermi degeneracy of the transitions 1596→0 and 992+606→0. In the spectrum of C_6D_6 only a single band is found in this region which exactly corresponds to the transition 947+579 = 1526→0 (it is known from Raman spectra that the frequency 992 drops to 947 cm^{-1} in C_6D_6). This difference between C_6H_6 and C_6D_6 is easily understood. The band 0→1480 (E_0), which is identified with the value of the 1596 vibration in the upper state, is not as strong as 0→520 (A_0^0). Hence the transition 1596→0 should be weaker than 992+606→0. The addition of a 992 vibration to the 606 makes the transition still stronger than the transition 606→0, according to the Franck-Condon principle (aside from Boltzmann factor). Now in light benzene the degeneracy and resultant mixing of the levels makes two bands appear with about the same intensity, whereas in C_6D_6 only the stronger 947+579→0 is found. These last bands, of course, have very weak intensity

[24] $\frac{\text{Intensity of } 0-2}{\text{Intensity of } 0-0}=\frac{1}{2}\left(\frac{\nu''-\nu'}{\nu''+\nu'}\right)^2$.

[25] In C_6D_6 the frequencies refer to the edges.

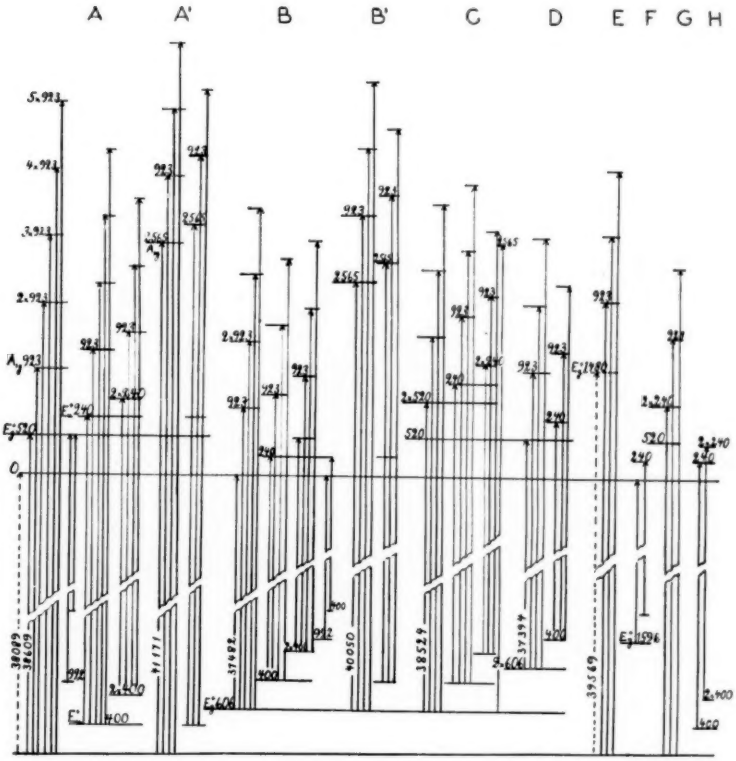


FIG. 3. Energy levels for benzene.

in absorption as a consequence of the Boltzmann factor.

Figure 3 contains a level scheme for the light benzene molecule and includes vibrational levels and transitions between them, on the basis of our analysis. The vibrational levels are drawn to scale, while the electronic level is not, as indicated by the interrupted lines. The 0,0 and a less certain transition are indicated by dotted lines. For simplicity not all observed members of the 923 cm^{-1} progression have been included. Wave numbers of all first members of the longer progressions have been added to facilitate the understanding of the diagram.

2. Rotational structure

As mentioned before, most bands look as if they were double-headed. The head on the long wave-length side is usually the stronger one, although all gradations appear. In the A_1^0 progression the short wave head is stronger and all but suppresses the other one. In some cases as in the progression $\nu = 38{,}089 + 2\times 520 - 606 + v_1 \times 923$, a third very weak head can be distinguished besides these two. Some fainter bands look single-headed, but this may be due to the fact that in this case only the strongest head can be seen on the plate. Although there is a possibility that the apparent structure of the bands is only accidental and that in reality the heads represent independent bands, we are rather inclined to ascribe the heads to true rotational structure as Henri has already done. We tentatively interpret the double heads as R and Q branches, and from the degradation of the bands towards the red we conclude that the R branch is the one on the short wave-length side. The different appearance of the rotational structure in different progressions indicates a coupling between vibration and rotation. The following simple treatment neglects such interaction.

The benzene molecule can be treated as a symmetrical top with two equal moments of inertia ($B=C$), the third one A having twice the value of each of the other two. A is the moment of inertia about the figure axis which is

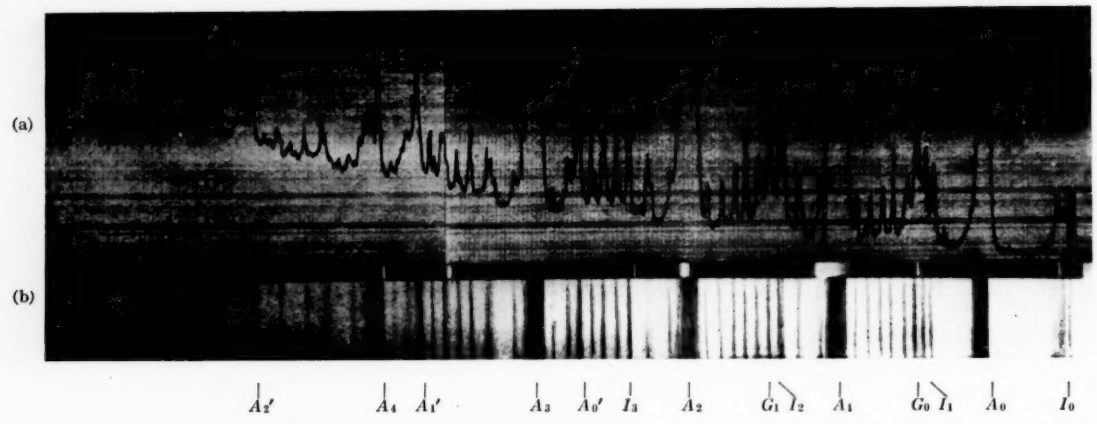


FIG. 4. Absorption spectrum of solid benzene at −259°C. Photograph taken from: A. Kronenberger, reference 28, p. 497.

perpendicular to the plane of the molecule. Hence the rotational energy can be represented solely in terms of the moment of inertia A:

$$E_r=\frac{\hbar^2}{2}\left[\frac{j(j+1)}{C}+k^2\left(\frac{1}{A}-\frac{1}{C}\right)\right]$$

$$=\frac{\hbar^2}{2A}[2j(j+1)-k^2].$$

The main branches P, Q and R are given by $\Delta j=-1,\ 0,\ +1$. Upon each branch are superimposed narrower p and r branches according to $\Delta k=\pm 1$ (perpendicular bands) or narrow q branches according to $\Delta k=0$ (parallel bands). The perpendicular bands correspond to changes of the transition moment in the x, y directions (displacement transforms like E_u^-) and are associated with vibrations of type E_g^+, whereas in parallel bands the change of the transition moment lies in the z direction (displacement transforms like A_{2u}), and these bands are connected with vibrations of type B_{1g}. We know from the vibrational analysis that all strong bands are of type E_g^+ and therefore are perpendicular bands.

The occurrence of double heads can be used for an estimate of the change of moment of inertia in the upper state, if we assume the interpretation as R and Q branches to be correct. Setting $k=0$, the change in A can be found in the usual way by inserting the observed value of 6 cm^{-1} for the distance from the R to the Q head. The result is $\Delta A=9\times10^{-40}$. Now from infra-red data[26] a value of 140×10^{-40} has been deduced for $B=C$, whereas 154×10^{-40} has been calculated[27] from the model. Deriving an average value of $A=300\times10^{-40}$ from these figures, one obtains 3 percent change in A and 1.5 percent in the internuclear C−C distance.

An independent method of estimating these changes is the application of the Franck-Condon principle to progressions of the totally symmetrical frequency 923 cm^{-1}, superimposed on any allowed transition. It is a general characteristic of the spectrum that in all such progressions the second member is the strongest, and the first and third are nearly equal in intensity. Taking the second one to be the strongest and using simple potential curves (instead of potential surfaces), it is possible to estimate the change in equilibrium distance from the relative position of the minima of the curves in the normal and excited states. The estimate, of course, is very rough and leads to $\Delta r=1.6\times10^{-10}$ cm, which means that for the C−C equilibrium distance of 1.4×10^{-8} cm in the ground state we obtain a change of 1.2 percent in the upper state. The good agreement with the other estimate is, of course, accidental, since both methods are very crude.

Interesting but small effects of anharmonicity seem to be present in some vibrations. However, a discussion should be postponed until the rotational structure is better understood.

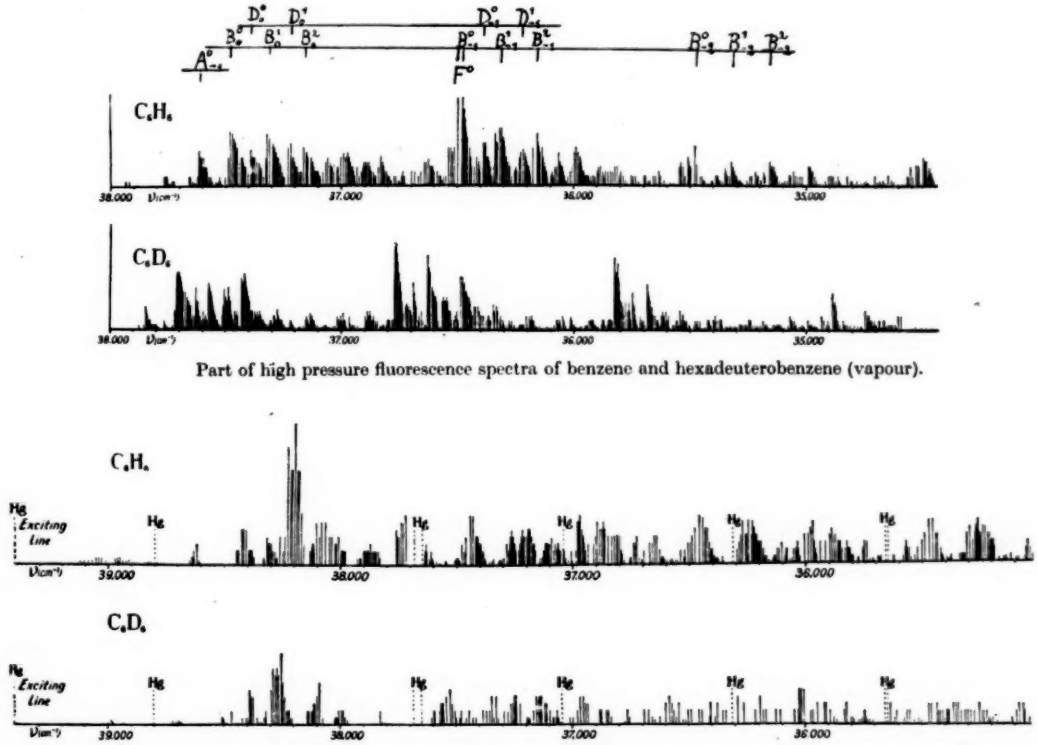
[26] C. E. Leberknight, Phys. Rev. **43**, 967 (1933).
[27] H. A. Stuart, *Molekülstruktur* (Julius Springer, Berlin, 1934), p. 78.

Absorption Spectrum of Solid Benzene at −259°C

Absorption spectra of solid benzene at very low temperatures have been investigated by Pringsheim and his co-workers.[28] Fig. 4 is a reproduction from Kronenberger's paper, but our notation has been used. It shows clearly the existence of a very strong progression with 923 cm^{-1} spacing in the spectrum. It is evident from the preceding sections that this progression is the one starting with the 0–1 transition of the 606 cm^{-1} vibration (520 cm^{-1} in the upper state), which is also the strongest progression in the vapor (A_1). There is, however, one striking difference in the appearance of the strong progression in the vapor and in the solid at −259°C. The absorption in the latter shows definitely a structure for each band, which has nothing to do with rotational structure (which would be absent at such a low temperature) and involves frequency differences of about 60 cm^{-1}. We believe that this splitting of each band into several bands is caused by superposition of crystal frequencies. They should lie at low temperatures on the short wave side of the main band. Hence the long wave edges of the strong bands have been used to fix their position.

Unlike the case of the vapor we should not have any 160 cm^{-1} progressions or 85 cm^{-1} displacements in combination with this strong progression, because bands originating from vibrational levels cannot occur at −259°C. This is in agreement with the experimental results. Apparent progressions of 160 cm^{-1} are undoubtedly of entirely different origin from that in the vapor, since the band heads in the solid *increase* in intensity towards longer wave-lengths, whereas in the gas they *decrease* towards longer wave-lengths as has already been noticed by Kronenberger. The spacing of 160 cm^{-1} in the solid which is also somewhat irregular must be accidental.

[28] P. Pringsheim and A. Kronenberger, Zeits. f. Physik **40**, 75 (1926); A. Kronenberger, *ibid.* **63**, 494 (1930).



Part of high pressure fluorescence spectra of benzene and hexadeuterobenzene (vapour).

Part of low pressure fluorescence spectra of benzene and hexadeuterobenzene (vapour) excited by Hg 2537 A.

Fig. 5. Schematic fluorescence spectra of C_6H_6 and C_6D_6. Taken from: C. K. Ingold, reference 22, p. 171.

We identify the first strong band observed in the solid at 38,348 cm^{-1} with our band at 38,609 which gives a shift of 261 cm^{-1} of the whole spectrum of the solid with respect to the gas. This leads to 37,828 cm^{-1} as position of the 0,0 band in the solid. There occurs a band in this region. We interpret it as the 0,0 band whose appearance is made possible in violation of the selection rules by the action on the benzene molecule of crystal forces. Actually this absorption extends from 37,797 to 37,907 cm^{-1}. Thus its long wave edge lies 31 cm^{-1} towards the red from the theoretical 0,0 band. It is not quite clear whether this shift is due to excitation of a crystal frequency in the initial state or whether it is caused by a resonance phenomenon between the electronic excitation of molecular units in the crystal. The 0,0 band should be accompanied by a progression of bands spaced from it in multiples of the totally symmetrical vibration 923 cm^{-1} (I series). Indeed such a series has been reported. Its first member I_0 lies at 37,842 cm^{-1}, i.e., within the absorption region of the 0,0 band.

Between A_2 and A_3 a new progression evidently starts with a rather strong band at 40,896 cm^{-1}. Its distance from the 0,1 band is 2548 cm^{-1}. The corresponding band in the vapor 41,171 had been interpreted as being due to one quantum of the totally symmetrical H vibration in the excited state superimposed on the 0–1 transition of E_g^+, 606.4 cm^{-1}. This interpretation led to a value of 2565 cm^{-1}, as compared with 2548 in the solid. We believe that this discrepancy is due to crystal forces.

There is another outstanding band between A_0 and A_1 upon which is superimposed a progression with spacing 923 cm^{-1}. This band lies at 38,816 cm^{-1}, and its distance from the 0,0 band is 988 cm^{-1}. The corresponding band 39,087 in the vapor had been interpreted before as belonging to the transition $0 \rightarrow 520 + 2 \times 240$. We take this explanation over for the solid. The slight discrepancy in numerical values can be understood in the same way as for the 2548 cm^{-1}. The bands of the four interpreted progressions have been marked in Fig. 4. They comprise all strong bands in the absorption spectrum of solid benzene at −259°C. No unambiguous interpretations can be given for the weaker bands, and we shall not present any such assignment.

Fluorescence Spectrum of Gaseous Benzene

1. Resonance fluorescence

The most recent detailed study of the resonance as well as of the high pressure fluorescence (see following section) has been given by Kistiakowsky and co-workers[2] and Ingold and co-workers.[29] To facilitate the discussion we reproduce from Ingold's most recent report on benzene[22] in Fig. 5 a schematic diagram of sections of both the resonance (benzene at 0.01 mm Hg) and high pressure fluorescence spectra (benzene at 25 mm Hg) of C_6H_6 and C_6D_6.

The resonance fluorescence has been excited with the mercury line 2537A = 39,409 cm^{-1}. According to simple theory one has to expect transitions from the level reached by absorption of the exciting line to all vibrational levels of the ground state permitted by symmetry. Unfortunately the wave-length of the exciting line does not coincide with that of a strong absorption band in light benzene. For that reason it cannot be decided which vibrations are excited by absorption. Probably several vibrational excitations occur. They give the spectrum a complicated appearance. It would certainly be helpful for the discussion of the whole resonance emission spectrum if the measurements could be repeated with another exciting line.

In C_6H_6 the mercury line lies between the absorption bands C_1^0 ($606 \rightarrow 2 \times 520 + 923$) and A_1^1 ($404 \rightarrow 240 + 520 + 923$), which is a region of weak absorption and therefore of small transition probabilities. In C_6D_6 the exciting line lies much closer to a strong absorption band ($579 \rightarrow 2 \times 497 + 878 - 140$), and we consider this as the reason for the less complicated appearance of the resonance emission of C_6D_6.

In both benzenes the excited level lies in the neighborhood of a vibrational level of symmetry E_g^+. We therefore should expect as the most prominent bands in resonance emission those leading to the totally symmetrical vibration A_{1g} and to the doubly excited E_g^+ vibration (the $\Delta v = \pm 1$ transitions being much more probable than the $\Delta v = 0$). Besides these, one should expect with weaker intensity any doubly excited

[29] C. K. Ingold and C. L. Wilson, J. Chem. Soc. pp. 941, 955 (1936); C. L. Wilson, J. Chem. Soc. p. 1210 (1936).

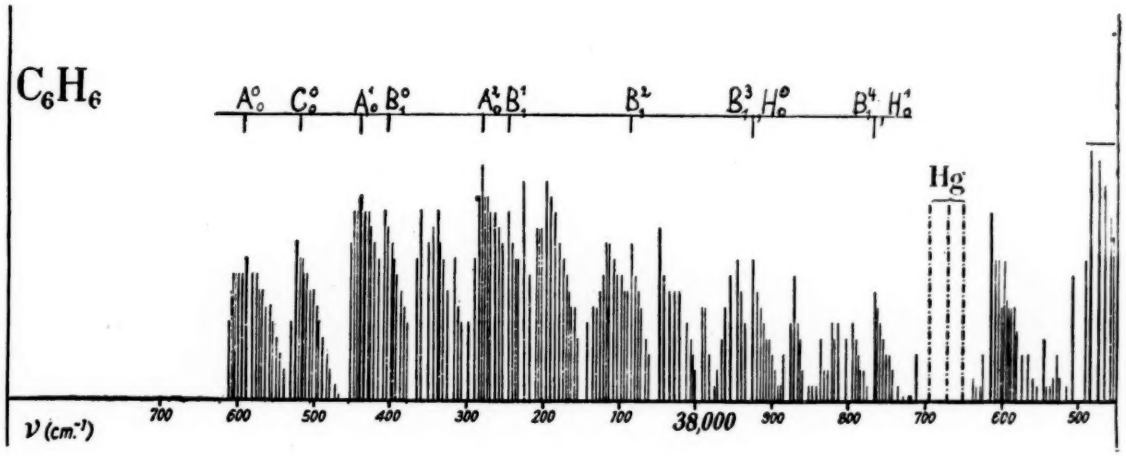


FIG. 6. Taken from: C. L. Wilson, reference 29, p. 1211.

nontotally symmetrical vibration of the ground state. Combinations of all these vibrations and progressions in the totally symmetrical vibrations can also occur with weak intensity.

Our theoretical expectations are in general agreement with observation, though the explanation of most of the complicated structure is uncertain or missing. The most prominent band peak in C_6H_6 at 38,197 cm^{-1} (1212 cm^{-1} distant from the exciting line) corresponds to the vibrational state 2×606 cm^{-1} and in C_6D_6 the band at 38,270 (distance 1139 cm^{-1}) corresponds to 2×579. The bands at 38,420 (distance 989 cm^{-1}) in C_6H_6 and at 38,465 (distance 944 cm^{-1}) in C_6D_6 are assigned to the 992 cm^{-1} and 947 cm^{-1} frequencies, respectively, as already reported by Ingold and Wilson.[29] Several other assignments are given by these authors, in which the displacement from the exciting line is twice the value of a nontotally symmetrical vibration in the fundamental state. Of course, additional recent information about the vibrations in the fundamental state[22] will change the picture to some extent. It seems, however, that at present not much can be added to the interpretation given for the resonance fluorescence.

2. High pressure fluorescence

The high pressure fluorescence spectrum of benzene and of heavy benzene can be described as groups of bands progressing in intervals of 992 cm^{-1} (947 cm^{-1} in C_6D_6) towards longer wavelengths. Most of the bands can be grouped, as in the absorption spectrum, into two major progressions, and on each of them another progression with a spacing of 160 cm^{-1} (140 cm^{-1}) is superimposed. The whole system is repeated with lower intensity shifted by about 85 cm^{-1} (82 cm^{-1} in C_6D_6) toward the red. For our analysis of the high pressure fluorescence spectrum we have used the measurements of Ingold and Wilson.[29] We refer here again to Fig. 5. In Fig. 6 is also reproduced the part of the high pressure fluorescence spectrum of C_6H_6 which lies in the region of strong absorption. The spectrum has been obtained at a benzene pressure of 0.1–0.3 mm Hg to which one atmosphere of nitrogen had been added. Our notation has been used.

Ingold and Wilson[29] have thought it necessary to assume three different electronic levels to explain the fluorescence spectrum. Since then Kistiakowsky and Solomon[11] interpreted two of their three band series as vibrational transitions superimposed on one electronic level at 37,482 cm^{-1}.

In our new analysis this interpretation has to be changed in the same way as for the absorption spectrum. There is one electronic level responsible for the whole system. It is a forbidden one (at 38,089 cm^{-1} in C_6H_6 and 38,292 cm^{-1} in C_6D_6). The bands at 37,473, 38,535 and 38,607 cm^{-1} are due to the vibrational transitions[30] $0\rightarrow606$, $2\times520\rightarrow606$ and $520\rightarrow0$, respectively. They are

[30] In fluorescence the arrows indicate the direction of emission.

identical with the bands B_0^0, C_0^0 and A_0^0 in the absorption spectrum (the three bands 37,709, 38,707 and 38,785 in C_6D_6 are due to the same transitions with corresponding vibrations). Superimposed on these vibrational transitions, which make the electronic transition allowed, one finds, as expected, progressions spaced 992 cm^{-1} toward the red. There are also progressions with a spacing of 160 cm^{-1} (140 cm^{-1} in C_6D_6) toward the red just as in absorption and likewise interpreted (n–n transition of the E_u^+ C vibration; in C_6H_6: $400-240=160$). Some of these progressions can easily be followed up to the fifth member.[31]

The band at 37,392 cm^{-1} is the first member of the D series ($520\rightarrow 2\times 606$); progressions with 992 and 160 cm^{-1} spacing are superposed on this band. Analogous bands are found in heavy benzene. The band group[32] at 36,900 cm^{-1} which is distant by about 1190 cm^{-1} from our 0,0 band may be correlated with the transition $0\rightarrow 1178$, where 1178 cm^{-1} is the smaller E_g^+ H vibration. This interpretation is borne out by the appearance of an outstanding band at about 37,430 cm^{-1} in heavy benzene which is 862 cm^{-1} distant from the 0,0 band and, on account of its intensity, cannot be included into any other progression. The frequency of the E_g^+ H vibration in C_6D_6 is known from Raman data to be 867 cm^{-1}.

In our notation negative subscripts have to be used for the main progressions. Thus only the first members A_0^n, B_0^n, $C_0^n\cdots$ coincide with strong absorption bands. That the B_1^n series is nevertheless present in fluorescence has already been remarked by Kistiakowsky and Solomon.[11] It is uncertain whether the bands at 37,930 and 37,765 are to be interpreted as B_1^3 and B_1^4 or as H^0 or H^1.

The explanation of relative intensities of the different band groups in the fluorescence spectrum is somewhat complicated. This is due to the fact that the bands are the result of a mechanism of excitation, subsequent collisions and reabsorption. As we should expect, the band series starting with B_0^0 ($0\rightarrow 606$ transition) is the strongest in the spectrum. In absorption we found the second member of the 923 cm^{-1} progression (878 cm^{-1} in C_6D_6) to be the most prominent in intensity. In the fluorescence of C_6H_6 as well as of C_6D_6, the second member of the corresponding 992 cm^{-1} progression (947 cm^{-1} in C_6D_6) is also by far the most outstanding band in the spectrum. In C_6H_6 there again appears the doublet (absent in C_6D_6) due to the Fermi degeneracy between the two E_g^+ C vibrations 1596 and $606+992$. The wavelengths of the corresponding bands B_{-1}^0, F^0 are 36,478, 36,497 cm^{-1}.

In Fig. 6 which shows the part of the fluorescence spectrum in the region of strongest absorption, there appear some slight irregularities in the relative intensities of the first members of the 160 or 140 cm^{-1} progressions. These irregularities can be understood as a result of the partial reabsorption of these fluorescence bands which coincide with the strongest absorption bands. The C and D series are weaker than the A and B series by what roughly corresponds to the Boltzmann factors.

Fluorescence measurements have also been undertaken in solid C_6H_6 at $-180°$ and $-259°C$ by Kronenberger.[28] He found two distinct progressions with spacings of about 990 cm^{-1}. One of them starts 600 cm^{-1} distant from our 0,0 band in the solid and obviously corresponds to the progression B_0, B_{-1}, $\cdots$, while the second progression originates at a distance of about 970 cm^{-1} from the 0,0 band and hence can be interpreted as I_{-1}, I_{-2}, $\cdots$. The fact that I_0 does not appear in fluorescence is probably due to reabsorption.

The above discussion shows that the fluorescence spectrum is in general agreement with the results obtained from the absorption spectrum.

One of the authors (A. L. S.) wishes to express his thanks to the Penrose Fund of the American Philosophical Society.

[31] Since in our analysis the 0,0 level is shifted by 606 cm^{-1} to shorter waves as compared to Kistiakowsky and Solomon (reference 11), the vibrational energy of the molecules will not have to be quite as high as these authors assumed.

[32] Although this band coincides with our D_0^3, its greater intensity suggests the overlapping of two bands.

The Extrapolation of Conductance Data for the Monovalent Nitrates and Iodates by Means of the Extended Onsager-Shedlovsky Equation

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It is shown that the extended Onsager-Shedlovsky equation $\Lambda_0=\Lambda_0'-BC-DC\log C$ where Λ and Λ_0 are the equivalent conductances at concentration C and at infinite dilution, Λ_0' is the limiting Onsager function $(\Lambda+\beta C^{\frac{1}{2}})/(1-\alpha C^{\frac{1}{2}})$, and B and D are disposable constants, serves for the extrapolation of conductance data for the monovalnt ∂nitrates and iodates. The anomalies in the conductance at low concentrations of these salts are due to the fact that the logarithmic term is for them relatively more important than it is for the corresponding chlorides.

AS AN extension to the limiting Onsager expression for the equivalent conductivity Λ of a strong electrolyte, Shedlovsky[1] in 1932 proposed the relation

$$\Lambda_0=(\Lambda+\beta C^{\frac{1}{2}})/(1-\alpha C^{\frac{1}{2}})-BC$$
$$=\Lambda_0'-BC, \qquad (1)$$

where Λ_0 is the equivalent conductance at infinite dilution, C is the concentration in equivalents per liter, α and β have their theoretical Onsager values, and B is a disposable constant. He showed that Eq. (1) represented reasonably closely the data for a number of 1−1 electrolytes (notably the alkaline halides) up to about $0.1N$, but that it failed for the alkaline nitrates and iodates. For the alkaline earth chlorides,[2] Shedlovsky and Brown modified Eq. (1) and used

$$\Lambda_0=\Lambda_0'-BC-DC\log C+EC^2, \qquad (2)$$

where B, D and E are disposable constants, the logarithmic term being consistent with the theoretical considerations of Onsager and Fuoss.[3] Subsequently, Shedlovsky, Brown and Mac Innes[4] found that in order to represent their newer and more accurate data for KCl, Eq. (2) rather than Eq. (1) was required.

Since deviations from limiting laws are usually the more serious the higher the ionic charge and the smaller the effective ionic radius, one might expect that Eq. (2) would be suitable for the monovalent nitrates and iodates as well, and that the so-called anomalies for these salts were simply due to the fact that for them the coefficient D was relatively large. This is apparently the case; Table I shows the comparison of the equivalent conductance computed by Eq. (2) and the experimental results of Shedlovsky[5] for potassium and silver nitrates at 25°C, while Table II gives a similar comparison for the data[6] in *International Critical Tables* for the chlorides, nitrates and iodates of sodium and potassium. The values of the disposable constants Λ_0, B and

TABLE I. 25°C; $\alpha=0.2274$; $\beta=59.79$.

	KNO_3			$AgNO_3$	
$10^4\cdot C$	Λ_{calc}	Λ_{obs}	$10^4\cdot C$	Λ_{calc}	Λ_{obs}
0.6982	144.18	144.21	0.2758	132.95	132.95
1.7613	143.70	143.66	0.7245	132.65	132.68
3.8888	143.05	143.02	1.0710	132.48	132.52
5.8651	142.60	142.65	3.5387	131.71	131.62
8.6853	142.07	142.01	4.6704	131.43	131.50
12.119	141.54	141.57	7.5380	130.88	130.86
16.468	140.98	140.95	10.026	130.50	130.49
24.219	140.15	140.21	12.297	130.18	130.14
36.724	139.09	139.12	14.530	129.90	129.90
50.00	138.19	138.48	29.054	128.49	128.48
100.00	135.86	135.82	50.00	127.05	127.20
	$\Lambda_0=144.99$		100.00	124.74	124.75
	$B=446$			$\Lambda_0=133.43$	
	$D=215$			$B=259$	
				$D=113$	

[1] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1405 (1932).
[2] T. Shedlovsky and A. S. Brown, J. Am. Chem. Soc. **56**, 1066 (1934).
[3] L. Onsager and R. Fuoss, J. Phys. Chem. **36**, 2689 (1932).
[4] T. Shedlovsky, A. S. Brown and D. A. Mac Innes, Trans. Electrochem. Soc. **66**, 165 (1934).
[5] T. Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932). As recommended by Shedlovsky and Brown (reference 2), his observed values have all been increased by 0.03 percent.
[6] The data for all six salts as recorded in *International Critical Tables* are uniformly 0.15 percent less than the results of Kohlrausch as recalculated by Noyes and Falk (A. A. Noyes and K. G. Falk, J. Am. Chem. Soc. **34**, 454 (1912)); in Table II, the values in *International Critical Tables* have all been increased by 0.12 percent, a correction which nearly restores them to their original values, and brings the entries for 1 N and 0.1 N KCl at 18° into agreement with Jones and Prendergast's recent absolute measurements on these two solutions (G. Jones and M. J. Prendergast, J. Am. Chem. Soc. **59**, 731 (1937)).

TABLE II. *18°C; $\alpha=0.225$; $\beta=50.3$.*

	$10^4 \cdot C$	5	10	20	50	100	200	Λ_0	B	D
KCl	Λ_{calc}	127.96	127.23	126.22	124.30	122.31	119.86	129.75	168.2	57.9
	Λ_{obs}	128.01	127.22	126.20	124.30	122.33	119.86			
NaCl	Λ_{calc}	107.08	106.40	105.45	103.67	101.81	99.52	108.75	147.0	45.6
	Λ_{obs}	107.08	106.40	105.44	103.66	101.84	99.52			
KNO_3	Λ_{calc}	124.30	123.54	122.46	120.36	118.08	115.08	126.11	125.2	70.7
	Λ_{obs}	124.31	123.52	122.47	120.35	118.07	115.10			
$NaNO_3$	Λ_{calc}	103.42	102.73	101.78	99.96	98.02	95.57	105.09	130.8	48.6
	Λ_{obs}	103.50	102.72	101.77	99.95	98.05	95.54			
KIO_3	Λ_{calc}	96.68	96.00	95.04	93.19	91.20	88.61	98.33	114.6	51.5
	Λ_{obs}	96.70	96.02	95.02	93.18	91.22	88.62			
$NaIO_3$	Λ_{calc}	75.79	75.17	74.29	72.62	70.85	68.58	77.32	114.2	41.9
	Λ_{obs}	75.81	75.17	74.29	72.61	70.84	68.56			

D used to compute the entries headed Λ_{calc} are given at the foot of the tables; the term EC^2 in Eq. (2) has been omitted since it makes only an insignificant contribution in the concentration ranges considered.

The agreement as a rule is excellent,[7] and is in general well within the limit of error of the experiments. It should be noted that in Table II the differences (Λ_0 for the potassium salt) $-$ (Λ_0 for the sodium salt) are 21.00, 21.02 and 21.01 for the chloride, nitrate and iodate, respectively, i.e., are (as predicted by the Kohlrausch rule) independent of the anion. The actual values of Λ_0 listed here, however, are considerably larger than those computed from the limiting ionic mobilities as given in *International Critical Tables*, even when the latter have been increased[6] by 0.12 percent; this is rather surprising, since the limiting mobilities were obtained presumably by some sort of extrapolation from the same data.[8] It should also be noted, once again in accord with theory,[2] that D is larger in every case for the potassium salt than for the corresponding sodium salt. The conclusion would seem to be that in extrapolating to infinite dilution conductance data for strong 1$-$1 electrolytes, Eq. (2) should be adopted as the normal form rather than Eq. (1).

[7] Shedlovsky's entries for 0.005 N KNO_3 and $AgNO_3$ as printed in his Table VII lie definitely off any large scale plot of the conductance data which includes both his results for the more dilute solutions (his Tables IV and V) and for the more concentrated (his Table VII). This is particularly apparent if values of Λ_0', computed from the entries in his tables, be plotted against C, or if $\Lambda+\beta C^{\frac{1}{2}}$ be plotted against $C^{\frac{1}{2}}$.

[8] The discrepancy varies from 0.15 for KCl to 0.29 for $NaIO_3$.

Infra-Red and Raman Spectra of Polyatomic Molecules

VI. Triborine Triamine, $B_3N_3H_6$*

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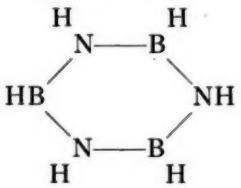
The Raman spectrum of liquid triborine triamine has been studied, and the infra-red absorption of the gas measured from 2.5 to 24.5μ. The molecule is assumed to be isoelectronic with benzene, belonging to the point group D_{3h}, and an assignment of fundamental frequencies is given, based upon this structure. A normal coördinate treatment has been made, and used to calculate the three inactive frequencies and the isotope shifts due to the B^{10} isotope. The agreement between calculated and observed values is satisfactory except for the nonplanar frequencies, where strong interactions between bonds attached to the aromatic ring in meta-positions are indicated. The fundamental frequencies of triborine triamine are compared with those of benzene; satisfactory correlation is obtained with the benzene frequencies given by Lord and Andrews. The frequencies of the triborine triamine are used together with structural data to calculate the thermodynamic properties of the substance.

TRIBORINE triamine, $B_3N_3H_6$, is one of the most interesting of the boron hydrides. Both chemical evidence and electron-diffraction studies[1] support a structure isoelectronic with benzene, having the configuration:



The present study was undertaken with a twofold purpose: we wished to study triborine triamine as a molecule containing the B−H and N−H linkages, and we also wished to compare its spectrum with that of benzene.

EXPERIMENTAL

Raman effect

The sample of triborine triamine used was prepared by Dr. Anton B. Burg at the University of Chicago. The material was introduced into a small Pyrex Raman tube (effective volume about 0.3 cc) by distillation *in vacuo*, and the entrance tube sealed off. The spectrum was excited by the blue-violet mercury lines (4047 and 4358A), and photographed with a Hilger E-439 spectrograph. The experimental arrangements, including those used in the polarization studies, have been previously described.[2] The best plates were measured with a comparator, using an argon comparison spectrum, and also microphotometered.

The observed frequencies of all lines found are given in Table I; the measurements are in most cases the averaged results from several plates. A few lines were measured only on the microphotometer tracings; the frequencies given for these lines are enclosed in parentheses. The values for the frequency shifts are collected in Table II, together with the intensity estimates and polarization characters of the lines. A microphotometer tracing of the spectrum is given in Fig. 1.

Polarization studies showed the four most intense lines to be polarized. These lines are marked in Table II, and are shown in the tracings of Fig. 2.

The intense line at 938 cm^{-1}, asymmetrical towards the high frequency side, is a partially

* This material was presented to the Division of Physical and Inorganic Chemistry of the American Chemical Society at Milwaukee, September, 1938.

** National Research Fellow in Chemistry.

[1] (a) A. Stock and E. Pohland, Ber. **59B**, 2215 (1926). (b) A. Stock and R. Wierl, Zeits. f. anorg. allgem. Chemie **203**, 228 (1931). (c) A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, 1933), Chapter XIV. (d) H. I. Schlesinger, L. Horvitz and A. B. Burg, J. Am. Chem. Soc. **58**, 409 (1936). (e) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.* **60**, 1296 (1938). (f) S. H. Bauer, *ibid.* **60**, 524 (1938).

[2] (a) J. T. Edsall, J. Chem. Phys. **4**, 1 (1936). (b) J. T. Edsall and E. B. Wilson, Jr., *ibid.* **6**, 124 (1938).

TABLE I. *Observed Raman frequencies.*

FREQUENCY, cm^{-1}, VAC.	INTENSITY*	ASSIGNMENT**
24181	0	524 *k*
(23997	0	708 *k*)
23854	3	851 *k*
23767	4	938 *k*
23660	0	856 *i*
23636	2	1069 *k*
23571	1	945 *i*
23477	?	1228 *k*
23444	0	1072 *i*
23227	0	−289 *e*
22793	0?	145 *e*
22650	3 *b*	288 *e*
22470	0?	525 *f*
22419	3	519 *e*
22230	0	708 *e*
22170	4 *vb*	2535 *k*
22140	1	798 *e*
22087	7	851 *e*
22000	9	938 *e*
21868	4	1070 *e*
21568	0	1370 *e*
21473	0	1465 *e*
21254	9	3451 *k*
21095	?	1843 *e*
21066	2	3450 *i*
20518	2	2521 *g*
20410	9 *vb*	2528 *e*
(19589	2	3450 *g*)
(19545	3	3450 *f*)
(19488	10	3450 *e*)

* *b* = broad; *vb* = very broad.
** The designation of the mercury lines is that of Kohlrausch: *e* = 22938, *f* = 22995, *g* = 23039, *i* = 24516, *k* = 24705 cm^{-1}, *in vacuo*. Frequencies enclosed in parentheses were measured on microphotometer tracings only.

resolved isotopic complex; the calculated shifts are discussed below (Fig. 5).

The lines at 23477 and 21095 cm^{-1} appeared very faintly on one plate only. Their reality is therefore doubtful, and in any case they are extremely weak shifts.

The Raman shift at 145 cm^{-1} is also of very doubtful reality. It is certainly a very weak line at best; moreover, it appeared almost at the edge of the dark background around the 4358A line. Since the small volume of material necessitated rather long exposures, this background was quite intense, making it very difficult to decide as to the reality of the 145 cm^{-1} line. Observations near the 4047A line were of no help, because of the weaker excitation and also because of the proximity of the 4078A line. The examination of plates taken with benzene in the Raman tube also failed to give a decisive answer.

Infra-red absorption

The infra-red spectrometer has been previously described.[3] The absorption was measured from 2.5 to 24.5μ, using rocksalt and KBr prisms in the appropriate regions of the spectrum. The cells used, 30 cm in length, were closed with KBr windows. The pressure of the triborine triamine was controlled by maintaining a bath around a small side-tube attached to the cell, the temperature of the bath being adjusted to give the vapor pressure desired.

The absorption curve is shown in Fig. 3. The frequencies of the absorption maxima are listed in Table III.

Certain of the bands require some comment. The reality of the shoulder at 480 cm^{-1}, and of the very weak band at 570 cm^{-1}, is somewhat doubtful; unfortunately we could not obtain pressures higher than 100 mm, which might have brought out these bands more definitely. The frequency 415 cm^{-1}, given for the lowest lying band, may be in error. This frequency lies near the long wave-length limit of our instrument, using the KBr prism; the effects of stray radia-

[3] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

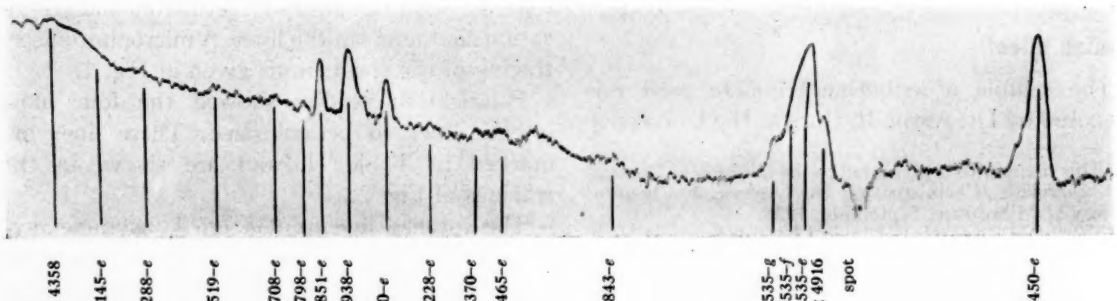


FIG. 1. Microphotometer tracing of the Raman spectrum of triborine triamine, excited by the Hg 4358A line.

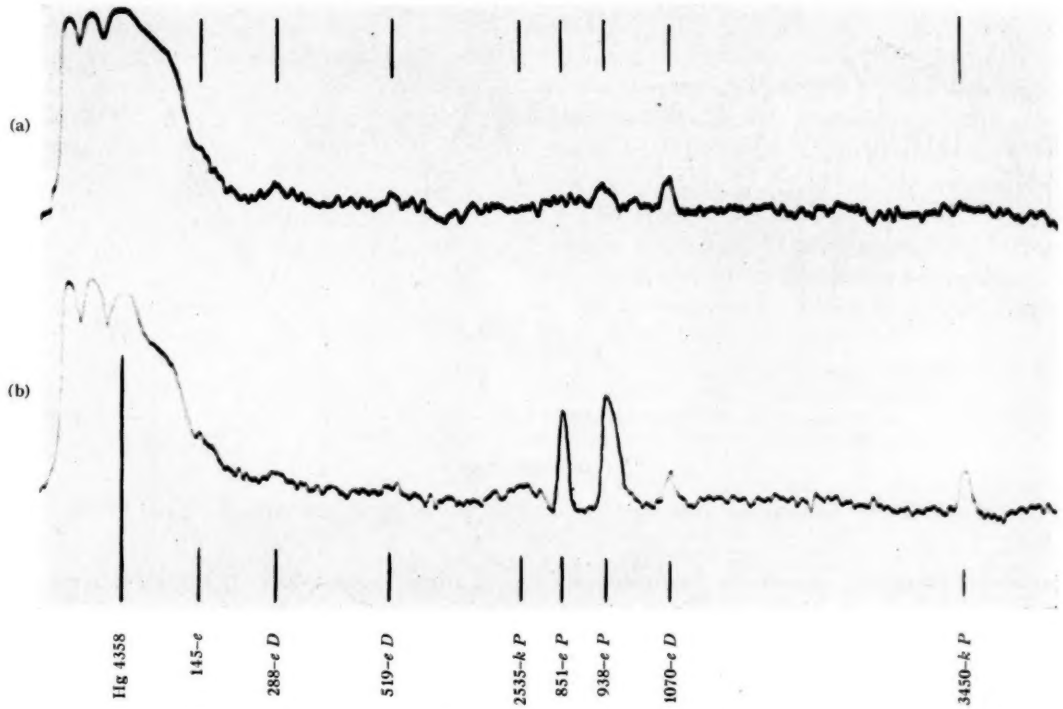


FIG. 2. Microphotometer tracings of the Raman spectrum of triborine triamine, excited by plane polarized light oriented (a) parallel and (b) perpendicular to the optical axis of the Raman tube. Polarized lines are marked P, depolarized lines, D.

tion become of greatly increased importance in this region, and may operate to shift the apparent absorption maximum of this band. The presence of a fairly strong absorption band at approximately 415 cm^{-1}, however, cannot be doubted.

The frequencies of the bands lying above 2000 cm^{-1} could not be determined as accurately as the lower frequencies, since the dispersion of rocksalt in this spectral region is quite low.

NORMAL MODES OF VIBRATION

Symmetry

Triborine triamine, isoelectronic with benzene, may be assigned to the point-group D_{3h}; the reduced representation for the internal vibrations then has the structure:[4]

$$\Gamma = 4A_1' + 3A_2' + 3A_2'' + 7E' + 3E'';$$

i.e., there are 20 distinct frequencies of which 10 are doubly degenerate; of these 20, 14 are planar vibrations and six involve motions perpendicular to the plane. This is entirely similar to the case of benzene, which has been treated by Wilson;[5] the similarity and the relations between the frequencies of the two molecules are shown in Table IV.

This table also gives the selection rules for the two molecules. It will be seen that those for

TABLE II. *Raman shifts, polarizations and assignments.*

FREQUENCY, cm^{-1}, VAC.	INTENSITY, POLARIZATION*	ASSIGNMENT	SYMMETRY
145	0?	—	—
288	2 *b*	Fund.	E''
519	3 *D*	Fund.	E'
708	1	Fund	E'
798	2	Fund.	E''
851	6 *P*	Fund.	A_1'
938	7 *P*	Fund.	A_1'
1070	5 *D*	Fund.	E''
1228	?	938+288=1226	E''
1370	1	525+850=1375	E'
1465	1	Fund.	E'
1843	?	917+938=1855	E'
2535	9 *vb P*	Fund.	A_1'
3450	10 *P*	Fund.	A_1'

* *b* = broad, *vb* = very broad, *P* = polarized, *D* = depolarized.

[4] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. 8, 317 (1936).

[5] E. B. Wilson, Jr., Phys. Rev. 45, 706 (1934).

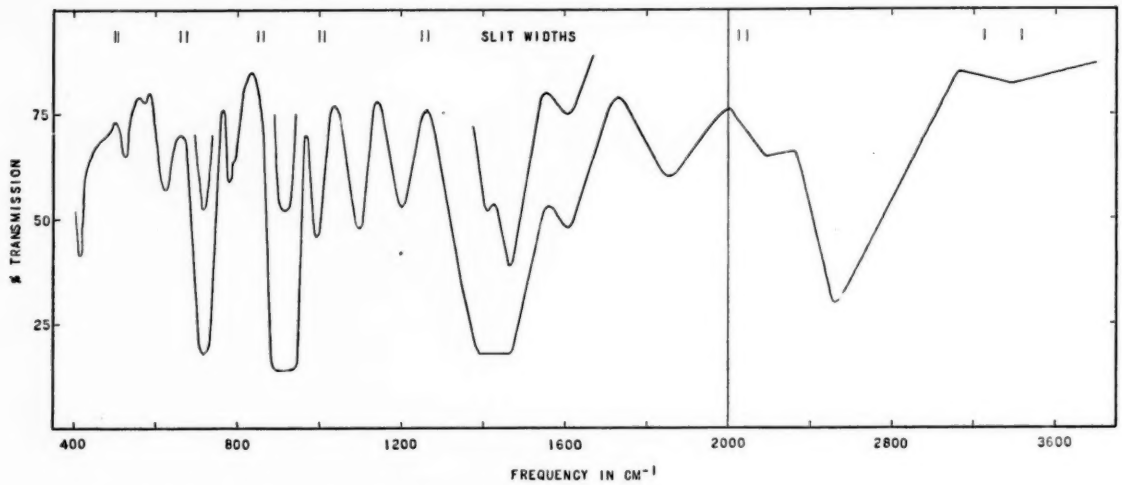


FIG. 3. Infra-red absorption of triborine triamine. Path length, 30 cm; pressures of 100 and 10 mm.

triborine triamine are unusually favorable for analysis, as they distinguish unambiguously between the various symmetry classes. The rules also allow all but three of the $B_3N_3H_6$ fundamentals to be directly observed, while only nine benzene fundamentals are observable.

Normal coördinate treatment

A normal coördinate treatment was carried out not only to investigate the magnitudes of the force constants in this molecule, but also to serve as a guide in the assignment of the fundamentals, and to enable calculation of the three completely inactive frequencies belonging to the class A_2'.

TABLE III. *Infra-red absorption bands and assignments.*

FREQUENCY, cm^{-1}	INTENSITY	ASSIGNMENT	SYMMETRY
415	40	Fund.	A_2''
480	?	——	——
525	20	Fund.	E'
570	5	$288^2=576$	$A_1'+E'$
622	30	Fund.	A_2''
717	70	Fund.	E'
778	30	$1070-288=782$	$A_1'+A_2'+E'$
790	5	$1098-288=810$	E'
917	100	Fund.	E'
990	40	$717+288=1005$	$A_1''+A_2''+E''$
1098	40	Fund.	A_2''
1199	35	$917+288=1205$	$A_1''+A_2''+E''$
1410	30	$717^2=1434$	$A_1'+E'$
1466	85	Fund.	E'
1610	30	Fund.	E'
1850	30	$917+938=1855$	E'
2174	10	$1466+717=2183$	$A_1'+A_2'+E'$
2519	60	Fund.	E'
3400	5	Fund.	E'

A simple valence-force potential function, without interaction constants,[6] was used; it was based on that proposed by Wilson[5] for benzene. Because of the greater number of bond types in triborine triamine, nine force constants were required to correspond to the six used for benzene.

The potential function for planar distortions is:

$$2V=K\Sigma_6(\Delta R_i)^2+q_B\Sigma_3(\Delta r_i)^2+q_N\Sigma_3(\Delta s_i)^2 +kR_0^2\Sigma_6(\Delta\alpha_i)^2+H_Br_0^2\Sigma_3(\Delta\beta_i)^2+H_Ns_0^2\Sigma_3(\Delta\gamma_i)^2.$$

Here R_i, r_i, s_i are the lengths of the ith B−N, B−H and N−H bonds, respectively, and R_0, r_0, s_0 are the equilibrium bond lengths. α_i is the ith B−N−B or N−B−N angle ($\alpha_0=120°$). $\Delta\beta_i$ measures the deviation of the ith B−H bond from the bisector of the N−B−N angle; $\Delta\gamma_i$ is the corresponding angle for the N−H bond ($\beta_0=\gamma_0=0$). K, q_B, q_N, k, H_B and H_N are the appropriate force constants.

For nonplanar distortions:

$$2V=h_Br_0^2\Sigma_3(\Delta\lambda_i)^2+h_Ns_0^2\Sigma_3(\Delta\mu_i)^2+\kappa d^2\Sigma_6(\varphi_i)^2.$$

Here $\Delta\lambda_i$ measures the deviation of the ith B−H bond from the plane of the adjacent B−N bonds, and $\Delta\mu_i$ is the corresponding N−H bond angle. φ_i is the angle of twist of the ith B−N

[6] Corrections to allow for the effect of hydrogen-hydrogen repulsion on the force constants H_N and H_B, analogous to those used by Lord and Andrews (reference 12) in their treatment of benzene, were not made. Recent evidence on hindered rotation of methyl groups seems to indicate that other types of interaction are more important than that calculated from present theory; we therefore considered it advisable to omit interaction forces altogether.

TABLE IV. *Symmetry classes of the normal vibrations of* $B_3N_3H_6$ *and* C_6H_6.*

$B_3N_3H_6(D_{3h})$		$C_6H_6(D_{6h})$	
PLANAR:			
$4\,A_1'$	(R, P)	$2\,A_{1g}$	(R, P)
		$2\,B_{1u}$	(In)
$3\,A_2'$	(In)	A_{2g}	(In)
		$2\,B_{2u}$	(In)
$7\,E'$	$(R, D; IR)$	$4\,E_{2g}$	(R, D)
		$3\,E_{1u}$	(IR)
NONPLANAR:			
$3\,A_2''$	(IR)	$2\,B_{2g}$	(In)
		A_{2u}	(IR)
$3\,E''$	(R, D)	$2\,E_{2u}$	(In)
		E_{1g}	(R, D)

* R, P = Raman active, polarized ($\rho \leq 6/7$); R, D = Raman active, depolarized ($\rho = 6/7$); IR = Infra-red active; In = Inactive.

bond, and d is the projection of the equilibrium B−N distance on a line perpendicular to the adjacent B−N bond ($d = R_0 \cos 30°$). h_B, h_N and κ are the appropriate force constants; κ arises from the partially double-bond character of the B−N bond, similar to that of the isoelectronic C−C bond in benzene.

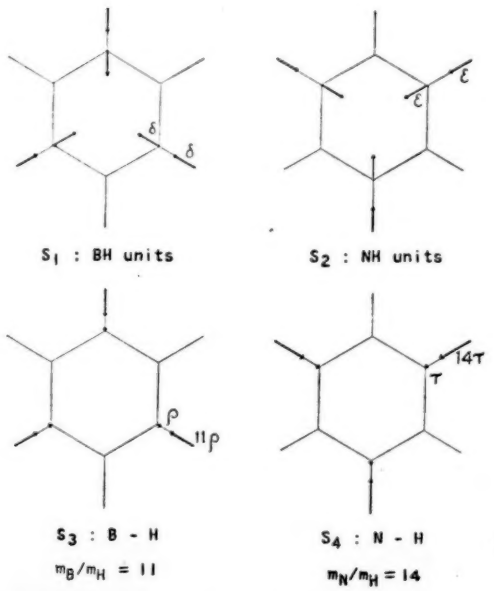


FIG. 4. Symmetry coördinates for the A_1' factor of the secular equation.

Approximate factoring

Using the experimentally justified concept of "bond frequencies" which remain approximately constant in different molecules, we may characterize the modes of vibration belonging to the various symmetry classes as shown in Table V.

The B−H and N−H stretching frequencies will lie much higher than the other frequencies of the molecule, and will interact with them to only a slight extent. In treating the A_1' and E' factors of the secular equation, we may choose symmetry coördinates such that one will involve B−H stretching, one N−H stretching, and the rest involve motions in which the BH and NH groups move as units. Such symmetry coördinates for the A_1' factor are shown in Fig. 4. It is then found that the interaction terms between the symmetry coördinates involving high frequency stretchings and the other coördinates of the same symmetry factor are comparatively small, and may be neglected in the first approximation. In the final treatment, perturbation methods may be applied;[7] the correction terms are small. This method of approximate factoring was useful in treating the A_1' and E' factors; it was indeed invaluable in the latter case, which was effectively reduced from an equation of the seventh order to a more manageable quintic.

TABLE V. *Types of vibrations in triborine triamine. The force constants involved in each symmetry factor are given in parentheses.*

PLANAR: A_1' (R, P)	A_2' (In)	E' $(R, D; IR)$
(K, k, q_B, q_N) N−H stretching B−H stretching ring distortion ring distortion	(K, H_B, H_N) N−H bending B−H bending ring distortion	$(K, k, H_B, H_N, q_B, q_N)$ N−H stretching B−H stretching N−H bending B−H bending ring distortion ring distortion ring distortion

NONPLANAR: A_2'' (IR)	E'' (R, D)
(κ, h_B, h_N) N−H bending B−H bending ring distortion	(κ, h_B, h_N) N−H bending B−H bending ring distortion

[7] J. H. Van Vleck, Phys. Rev. **33**, 484 (1929); O. M. Jordahl, *ibid.* **45**, 87 (1934); E. B. Wilson, Jr. and J. B. Howard, J. Chem. Phys. **4**, 260 (1936). We are indebted to Professor Wilson for suggesting the use of this type of symmetry coördinate and the application of the perturbation treatment to the resulting secular equation.

The frequency expressions which were obtained are too complicated to be reproduced here. The force constants involved in each of the symmetry factors are shown in Table V.

The Vibration Frequencies

The totally symmetric vibrations

In spite of the favorable way in which the selection rules discriminate between the various symmetry classes, a complete assignment cannot be made on this basis alone. In the first place, some of the E' frequencies, which should appear in both Raman and infra-red, are apparently too weak in the Raman effect to be detected; i.e., there are too few coincidences between Raman and infra-red. Moreover, certain combination frequencies appear with intensities comparable to those of the fundamentals.

For the totally symmetric frequencies (A_1'), there is no ambiguity. The four intense Raman lines with shifts of 851, 938, 2535 and 3450 cm^{-1} are all polarized, and are the only lines found to be polarized; they may therefore be assigned at once to the A_1' class.

The frequencies at 3450 and 2535 cm^{-1} obviously belong to the N−H and B−H stretchings, respectively. The N−H frequency lies somewhat above the values found for amines, which range around 3350 cm^{-1}; this is perhaps similar to the higher frequency of the C−H vibration in benzene, compared to the C−H frequencies in methyl groups. The B−H frequency of 2535 cm^{-1} may be compared with the Raman line recently found in B_2H_6 by Anderson and Burg,[8] at 2523 cm^{-1}. The assignment proposed by these authors postulates a resonance splitting which gives this line and one at 2102 cm^{-1}; on this basis, the true B−H fundamental in B_2H_6 would lie considerably lower than that in triborine triamine. The diatomic molecule BH has, in the ground state ($A^1\Sigma^+$), $\omega_e = 2230$ cm^{-1}; in the $C^1\Pi$ excited state, $\omega_e = 2450$ cm^{-1}.[9]

The assignment of these four lines permitted the evaluation of the constants K, k, q_B and q_N (see Tables VI and VII); these constants were used in the E' and A_2' factors also.

[8] T. F. Anderson and A. B. Burg, J. Chem. Phys. **6**, 586 (1938).

[9] H. Sponer, *Molekulspektren* (Berlin, 1935), pp. 24–25.

The B^{10} isotope effect

The vibration of frequency 938 cm^{-1} involves relatively large motions of the BH groups, and is therefore sensitive to changes in the mass of the boron atom. The B^{10}/B^{11} ratio is about $\frac{1}{4}$; hence the relative abundance ratios for the four molecules $B_3{}^{11}N_3H_6$, $B^{10}B_2{}^{11}N_3H_6$, $B_2{}^{10}B^{11}N_3H_6$, $B_3{}^{10}N_3H_6$, on a random chance basis, are

TABLE VI. *The fundamental frequencies, calculated and observed, of triborine triamine and of benzene, in* cm^{-1}.

$B_3N_3H_6$ Frequency			C_6H_6 Frequency			
Symmetry	Observed	Calc'd	Observed	Calc'd (L and A)†	Assigned (Ing.)**	Symmetry
A_1'	851	845	992	993	(992)	A_{1g}
	938	940	—	1008	766	B_{1u}
	2535	2544	3061	3061	(3061)	A_{1g}
	3450	3463	—	3063	3062	B_{1u}
E'	525	537	606	608	(606)	E_{2g}
	717	745	1037	1030	(1037)	E_{1u}
	917	954	1178	1170	(1178)	E_{2g}
	1466	1320	1485	1480	(1485)	E_{1u}
	1610	1593	1596	1645	(1596)	E_{2g}
	2519	2544	3047	3107	(3047)	E_{2g}
	3400	3463	3080	3080	(3080)	E_{1u}
A_2'	—	800	—	1145	1145	B_{2u}
	—	1110	—	1190	1240	A_{2g}
	—	1650	—	1854	1720	B_{2u}
E''	288	283	(406)*	406	(low)	E_{2u}
	798	790	850	850	(849)	E_{1g}
	1070	1086	—	1160	890	E_{2u}
A_2''	415	403	—	538	(low)	B_{2g}
	622	756	671	783	(671)	A_{2u}
	1098	1278	—	1520	1000	B_{2g}

* Lord and Andrews' assignment, assuming that intermolecular forces in the liquid break down the selection rules and allow this forbidden line to appear.

** Reference 9; frequencies in parentheses are those observed; others are from combination assignments and reduced mass calculations.

† Reference 10; frequencies calculated from Wilson's equations.

TABLE VII. *Force constants for triborine triamine and for benzene.**

$B_3N_3H_6$ Constant	Value (10^5 dyne/cm)	C_6H_6 Constant	Value (10^5 dyne/cm)
Planar			
K (B−N stretching)	6.300	K (C−C stretching)	7.58
k (B−N−B or N−B−N bending)	0.525	k (C−C−C bending)	0.65
H_B (B−H bending)	0.35	H (C−H bending)	0.76
H_N (N−H bending)	0.65		
q_B (B−H stretching)	3.423	q (C−H stretching)	5.05
q_N (N−H stretching)	6.524		
Nonplanar			
κ (B−N torsion)	0.10	κ (C−C torsion)	0.23
h_B (B−H bending)	0.23	h (C−H bending)	0.34
h_N (N−H bending)	0.42		

* Constants for benzene from Lord and Andrews, reference 6.

50 : 40 : 10 : 1. The isotopic shifts are 15, 27, and 38 cm^{-1}.[10] The comparison given in Fig. 5 justified the assignment of the high frequency satellites of the 938 cm^{-1} Raman line to the various isotopic molecules involving B^{10}; the isotopic lines were not completely resolved with our instrument.

The E' and A_2' vibrations

The frequencies of the E' class should appear in both infra-red and Raman effect. The infra-red bands at 2519 and 3400 cm^{-1} are obviously to be assigned to the E' B−H and N−H stretchings (see Table V). These frequencies are either too weakly Raman active to appear, or they are overlaid by the more intense lines of the A_1' fundamentals. (The discrepancy in the frequencies is within the rather large error of the infra-red values in this region of the spectrum.)

There are three obvious coincidences at 525, 717 and 1466 cm^{-1}; these may also be assigned to E' vibrations. Their intensities mark them as fundamentals. There is also an apparent coincidence between the Raman frequency of 798 and the infra-red frequency of 790 cm^{-1}. Here, however, the infra-red band is so extremely weak, being indeed a mere shoulder on the rather weak 778 cm^{-1} band, that it cannot reasonably be assigned to a fundamental. It seems more probable that the fairly intense Raman line is due to a fundamental active only in the Raman effect, while the infra-red shoulder is to be assigned to some combination tone. There may also be some question of coincidence between the Raman line at 1070 cm^{-1} and the infra-red band at 1098 cm^{-1}; the discrepancy of 28 cm^{-1} seems rather large, however, and we have preferred to assign these frequencies to separate vibrations.

There are still two E' frequencies to be assigned. The very strong infra-red band at 917 cm^{-1} is surely a fundamental, and may satisfactorily be assigned to this class; it will appear below that the only alternative assignment, to the A_2'' class, is quite unsatisfactory.

To fix the remaining E' frequency, we may use the constants already determined, K, k, q_B and q_N, in the E' factor of the secular equation; these serve to fix one E' frequency at about 1600 cm^{-1}, for any possible values of H_B and H_N. We there-

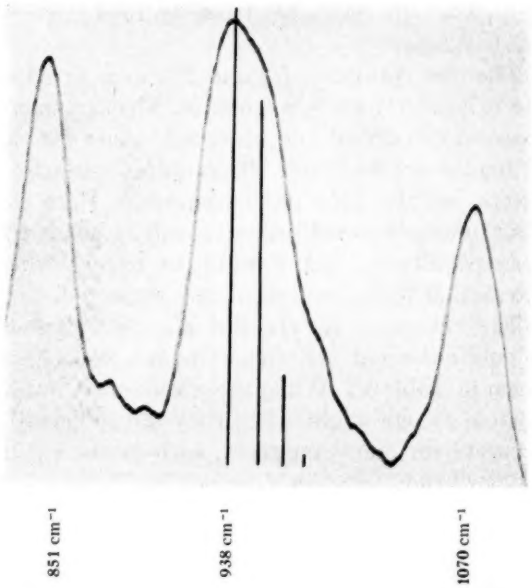


FIG. 5. Enlarged microphotometer tracing of the 938 cm^{-1} Raman line, compared with the components calculated for isotopic molecules. Heights of the calculated lines correspond to the relative intensities to be expected.

[10] The isotopic shifts are easily calculated by regarding the change of mass as a perturbation in the kinetic energy, and writing the secular equation for the isotopic molecule in terms of the normal coördinates of the "unperturbed" molecule. The secular equation for the "perturbed" frequencies, λ, is

$$|\lambda_k^0\delta_{kl}-\lambda[\delta_{kl}+\sum_i \Delta m_i(l_{ik}\cdot l_{il})]|=0.$$

Here the subscripts k and l refer to normal modes of vibration which are of approximately the same frequency and are in the same symmetry class of the *isotopic* molecule. λ_k^0 is the frequency parameter ($\lambda_k^0=4\pi^2c^2\omega_k^2$) for the kth mode of the unperturbed molecule; Δm_i is the change of mass of the ith atom; l_{ik} is the *vector* displacement of the ith atom in the kth mode, normalized to

$$\sum_i m_i l_{ik}^2=1$$

and δ_{kl} is the Kronecker symbol. In the cases $B^{10}B^{11}{}_2N_3H_6$ and $B^{10}{}_2B^{11}N_3H_6$, molecules of symmetry C_{2v}, the 917 cm^{-1} frequency (E' of D_{3h} in $B^{11}{}_3N_3H_6$) and the 938 cm^{-1} frequency belong to the same symmetry class, A_1 of C_{2v}; hence these two modes must be considered and the secular equation for the isotopic frequency is a quadratic. In the $B^{10}{}_3N_3H_6$ case, the isotopic molecule also has the symmetry D_{3h}, and only the 938 cm^{-1} frequency need be considered. The secular equation reduces to

$$\lambda_k^0-\lambda(1+\sum_i \Delta m_i l_{ik}^2)=0$$

or, changing over to frequencies instead of the parameters λ,

$$\frac{d\nu}{\nu}=-(\tfrac{1}{2})\sum_i \Delta m_i l_{ik}^2.$$

This last result has been given by E. Teller (*Hand- und Jahrbuch der chemischen Physik* (Leipzig, 1934), Vol. 9, p. 142 *et seq.*). We are indebted to Professor Wilson for the results given above.

fore assign the infra-red band at 1610 cm^{-1} to this frequency.

The new constants H_B and H_N were fitted to the 717 and 917 cm^{-1} frequencies. The agreement between calculated and observed values for the E' fundamentals (Table VI) is quite satisfactory except for the 1466 cm^{-1} frequency. Here the error amounts to ten percent; such agreement is perhaps all one has a right to expect when interaction terms are completely neglected.

The constants K, H_B and H_N were used to calculate the inactive planar frequencies (A_2') as given in Table VI. While these values are not as reliable as one might wish, they are sufficiently accurate for many purposes, such as the calculation of thermodynamic properties.

The nonplanar vibrations

Turning to the E'' class, which should give depolarized Raman lines, we assign the 798 cm^{-1} line, discussed above, to this class. The 288 and 1070 cm^{-1} lines obviously belong to the E'' group, and the assignment is thus completed. From these three frequencies the constants κ, h_B and h_N were determined.

The frequencies of the A_2'' vibrations were then calculated to be 403, 756 and 1278 cm^{-1}. The infra-red band at 415 cm^{-1} may at once be assigned to the low frequency A_2'' vibration. We assigned the 1098 cm^{-1} band to the high frequency N−H bending vibration, being led to this choice by the fact that we could find no other really satisfactory assignment for this band; other possible choices for the A_2'' fundamental (the 1199 and 1410 cm^{-1} bands) could be assigned as combination tones. The large discrepancy between the calculated and observed values will be discussed below.

For the B−H bending vibration, of calculated frequency 756 cm^{-1}, we may consider the bands at 622 and 778 cm^{-1}; it seems unlikely that the frequency could lie near 717 cm^{-1} and be so completely masked by the E' fundamental that no asymmetry of the band would result. Since the N−H bending frequency was found to lie considerably below the calculated value, it may reasonably be supposed that a similar discrepancy would exist in the case of the B−H bending frequency; we therefore chose the 622 cm^{-1} band for this assignment. This choice receives *a posteriori* support from the close analogy between the out-of-plane B−H, N−H and C−H bending frequencies, which appears when we compare the benzene spectrum with that of triborine triamine.

The calculated and observed fundamentals are collected in Table VI; the force constants are in Table VII. The assignments of all the observed frequencies are given in Tables II and III. Satisfactory assignments were found for all the observed frequencies except the Raman line at 145 cm^{-1} and the infra-red band at 480 cm^{-1}; both these frequencies are extremely doubtful, and are in fact included merely for the sake of completeness.

It cannot be claimed that all alternative assignments have been rigorously excluded in the above argument. However, in exploring the various alternatives, we have been unable to find any other assignment which was at all acceptable, unless we postulated that the higher E'' frequencies do not appear. While this possibility cannot be rejected, it would make a complete assignment impossible, and the assignment given above is in any case more reasonable and satisfactory than the alternatives.

Comparison with Benzene

Assignments of all the fundamental frequencies of benzene, both observable and inactive, have been made by Ingold and his co-workers[11] and by Lord and Andrews.[12] The two sets of assigned fundamentals, which agree quite closely, are compared with the corresponding fundamentals of triborine triamine in Table VI. The force constants are compared in Table VII.

Figure 6 shows graphically the comparison given in Table VI. The correlation between the two spectra is, on the whole, quite pleasing. The correspondence of the N−H and B−H stretching frequencies needs no comment.

With respect to the lower frequencies, involving bending vibrations and ring distortions, in almost all the cases in which both the benzene and the $B_3N_3H_6$ frequencies are observed, the benzene frequency is the higher.[13] The benzene

[11] C. K. Ingold *et al.*, J. Chem. Soc. 912 (1936).

[12] R. C. Lord, Jr., and D. H. Andrews, J. Phys. Chem. **41**, 149 (1937).

[13] The single exception occurs in the E' class, where the $B_3N_3H_6$ frequency at 1610 is slightly higher than that of C_6H_6 at 1596 cm^{-1}. This may be looked upon as a case of

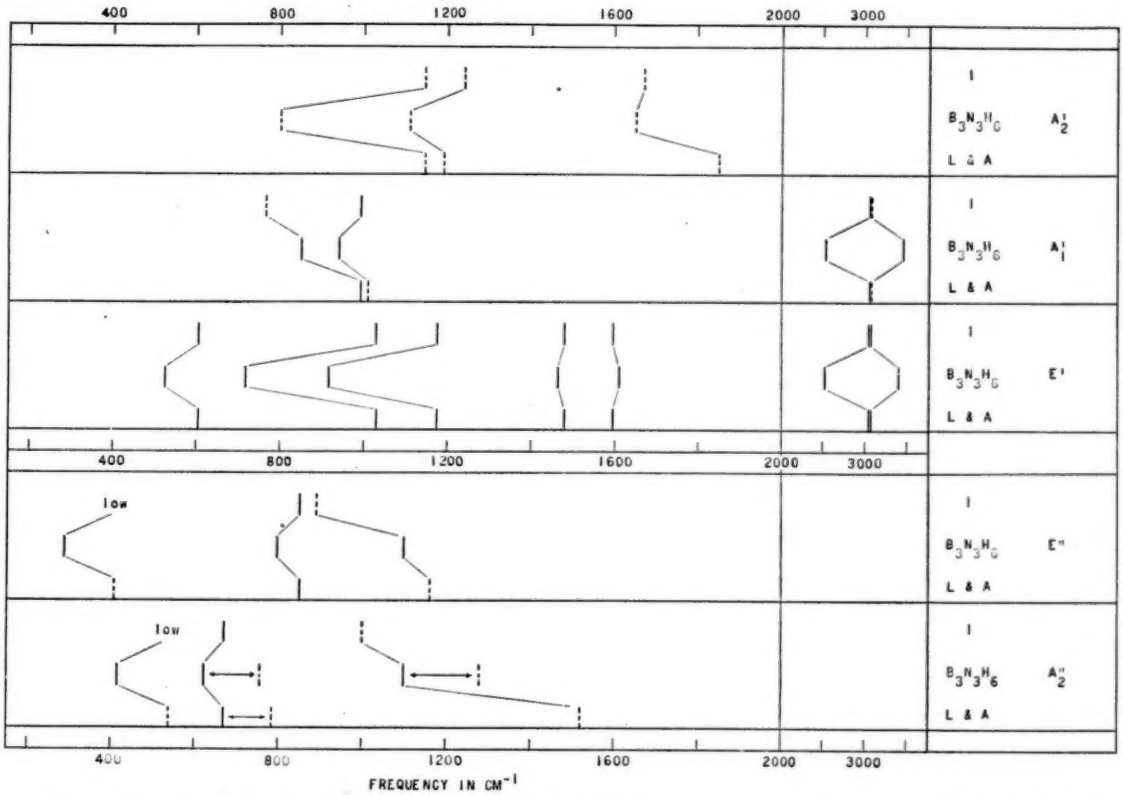


FIG. 6. Comparison of the fundamental frequencies of triborine triamine and benzene. Observed frequencies are represented by solid lines, calculated frequencies by broken lines. In each symmetry class of $B_3N_3H_6$, the benzene fundamentals proposed by Ingold and co-workers are plotted above the corresponding frequencies of $B_3N_3H_6$, and those proposed by Lord and Andrews below; corresponding fundamentals are connected. In the A_2'' class, it will be noted that both observed and calculated values are plotted for two $B_3N_3H_6$ and one C_6H_6 fundamentals.

values calculated by Lord and Andrews also lie above the corresponding observed $B_3N_3H_6$ values, while those given by Ingold and his collaborators are lower in three instances (A_1', 766; E'', 890; A_2'', 1000). From the instances in which the frequencies of both molecules are observed, it would seem reasonable to suppose that the benzene frequencies would lie higher in all cases; from this viewpoint, the $B_3N_3H_6$ spectrum offers indirect evidence in favor of Lord and Andrews' set of benzene fundamentals rather than those of Ingold and his co-workers.

The correlation between the lowest nonplanar frequencies of the two molecules (A_2'' and E'') is quite satisfactory, and supports Lord and Andrews' assignment of the weak 406 cm^{-1} Raman line in liquid benzene to the forbidden E_{2u} fundamental.

The nonplanar bending frequencies of the C−H bond in benzene and of the B−H and N−H bonds in triborine triamine present a curious parallelism. For each type of bond, this bending is involved in fairly pure form in a pair of vibrations of which one is infra-red, the other Raman active; thus in benzene the 850 and 671 cm^{-1} frequencies involve the C−H bond, and in triborine triamine the 798 and 622 cm^{-1} frequencies involve the B−H bond and the 1070 and 1098 cm^{-1} frequencies, the N−H bond. In each case, the infra-red active vibration bends opposite bonds in the *same* direction, while the Raman active vibration bends opposite bonds in *opposite* directions. Thus in benzene, in the infra-red active motion the carbon ring oscillates

classical resonance; the benzene fundamentals at 1485 and 1596 cm^{-1} are in different symmetry classes and cannot interact, while in $B_3N_3H_6$ the corresponding vibrations can interact to cause a slight spreading of the frequencies, observed at 1466 and 1610 cm^{-1}. It should also be remembered that the value 1596 cm^{-1} (C_6H_6) is the mean of a quantum-mechanical resonance doublet, and may itself be somewhat in error.

against the hydrogen ring along the sixfold axis; in the Raman active motion, the two rings rock against each other, rocking about one of the twofold axes. (See numbers 11 and 10*a* in Fig. 3 of reference 5.) The potential functions used for the two molecules neglect possible interactions between opposite bendings. With this assumption, the force constant (e.g., h_B) was fitted to the Raman frequency (798 cm^{-1}) and then used to calculate the value of the infra-red frequency (756 cm^{-1}). The discrepancies between these calculated values and the observed infra-red frequencies amount to 16, 18 and 14 percent for the C−H, B−H and N−H vibrations, respectively.

These large discrepancies indicate quite strong interactions between opposite bonds attached to an aromatic ring. Moreover, while the benzene discrepancy could be accounted for by postulating such interaction between bonds attached in the *para* positions, the discrepancies in triborine triamine make it necessary to assume interactions between bonds attached in the *meta* positions. It is unfortunate that the inactive character of the A_2' vibrations precludes investigation of the possible meta-position interactions in the planar bending vibrations.

Thermodynamic Properties

The entropy, free energy function, and heat capacity for triborine triamine (perfect gas at 1 atmos. pressure) were calculated at several temperatures by standard statistical methods.[14] In calculating the translational and rotational contributions, the following values were used: atomic weights, 10.82, 14.008, 1.008 for B, N and H, respectively; symmetry number, 6; bond angles (B−N−B, B−N−H, etc.), 120°; interatomic distances,[1f] B−N, 1.44, B−H, 1.20, N−H, 1.02A. The entropy due to nuclear spin was neglected, in accordance with the usual convention of "virtual" entropy. In calculating the vibrational contributions, the observed fundamental frequencies as listed in Table VI were used for all but the three inactive fundamentals; the calculated values for these frequencies were used of necessity. The results of the calculations are given in Table VIII.

[14] L. S. Kassel, Chem. Rev. **18**, 277 (1936).

Table VIII. *Thermodynamic properties of triborine triamine, calculated for the perfect gas at 1 atmos. pressure, in cal./mole/degree. Values of the universal constants were taken from the Int. Crit. Tab.*

T, °K	S^0	$-(F^0-E_0^0)/T$	C_p^0
298.1	73.7	60.4	23.3
326 (b.p.)	75.8	61.5	25.3
350	77.7	62.6	27.1
400	81.5	64.8	30.4
500	88.9	68.7	36.0
600	95.9	72.6	40.5
700	102.5	76.6	44.2
800	108.5	80.2	47.2
900	114.2	83.6	49.6
1000	119.6	87.0	51.8

The correctness of these thermodynamic values rests entirely upon the correctness of the vibrational assignment used; it is therefore impossible to set an absolute "limit of error." However, unless the vibrational assignment is seriously in error, the principal sources of uncertainty are the three calculated frequencies of the A_2' class. Such errors would be unlikely to change the thermodynamic values by more than 0.5 percent in the most unfavorable case.

Vapor pressure data[1a, 1c] were combined with the thermodynamic values for the gas to give the following data for the liquid: $S^0_{298}(l)=51.0$, $S^0_{326}(l)=53.4$ (326°K is the boiling point), $[(F^0-E_0^0)/T]_{298}(l)=-62.5$ cal./mole/degree.

The use of analytical expressions for the thermodynamic properties as functions of the temperature has been discussed by Murphy[15] and by Linnett and Avery.[16] The following expressions are satisfactory over the temperature range of Table VIII:

$$S^0(g)=-19.724+32.588\log T+0.04164T$$
$$-[(F^0-E_0^0)/T](g)=-33.877+2201.1(1/T)+32.588\log T+0.02082T$$
$$S^0(l)=-25.062+24.582\log T+0.05119T$$
$$-[(F^0-E_0^0)/T](l)=-35.738+8869.2(1/T)+24.582\log T+0.02559T.$$

We wish to express our thanks to Dr. Anton B. Burg for the sample of triborine triamine which made this study possible, and to Professor E. B. Wilson, Jr., who suggested this project and has contributed many helpful suggestions throughout the course of the investigation.

[15] G. M. Murphy, J. Chem. Phys. **5**, 637 (1937).
[16] J. W. Linnett and W. H. Avery, J. Chem. Phys. **6**, 686 (1938).

Liquid Structure and Entropy of Vaporization

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The entropies of vaporization of a number of liquids to the same vapor volume are compared and show evidence that more or less ordered arrangements in liquids can result not only from (a) chemical bonds, and (b) dipole orientation but also from (c) geometrical form. This last effect alone may suffice to cause significant departures from the entropy of forming a regular solution.

IN 1884 Trouton[1] announced the well-known and exceedingly useful rule that the heat of vaporization of a liquid divided by its absolute boiling point has the same value for all "normal" liquids. It was later recognized that there is a drift in this quotient with increasing boiling point and Nernst,[2] Bingham,[3] Forcrand[4] and others have given empirical formulas to take this into account. Upon examining this relationship in 1915,[5] I noticed that the curves obtained by plotting log p against log T, whose tangents at any point represent the entropy of vaporization, ΔS, divided by the gas constant, R, had equal slopes, not at any uniform pressure, such as 760 mm, but rather when compared at intercepts with any straight line of unit slope, i.e., log $p=\log T+\text{const}$. The meaning of this becomes clear if we remember that for any perfect gas $\log p=\log T+\log Rc$, where c is the concentration; hence these lines represent equal vapor concentrations rather than pressures as in Trouton's rule. It holds with good approximation for normal liquids all the way from nitrogen to silver. Helium and hydrogen alone are beyond its range due to quantum considerations. Much use has been made of it and several have discussed its theoretical basis.[6] It is, perhaps, a relation that may be deduced quite as convincingly as derived simply by contemplating the pure thermodynamic equation, $\Delta S=\Delta V(dp/dT)$ for ΔV is hardly influenced by the volume of the liquid, and it is reasonable that the values of ΔS for various normal liquids should be the same when we choose the temperatures so that the vapor volumes are the same, selecting, of course, values for which the pressures are sufficiently low for the vapors to obey the gas laws. The equality of dp/dT under these conditions is rather more than a good hunch.

At the recent symposium on intermolecular action when the accuracy of the rule was mentioned, I remarked that I should not want it to be too accurate, and the following paragraphs show the results of an examination of deviations from it on the part of liquids usually considered quite normal. One may expect that any factor tending to produce order in a liquid would diminish its entropy and hence increase the entropy of the transition to vapor, where any mutual ordering effect of the molecules disappears. The factors tending to produce order may be classified as chemical association, dipole orientation and geometrical shape. The large effect of the first has long been evident in the positive deviations from either the Trouton or the Hildebrand rule in the case of such liquids as water, ammonia and alcohols. The second factor is well recognized, although it often exerts a rather small effect if the dipole is buried. The chief purpose of this study was to bring to light the third factor, particularly in consequence of recent discussions[7] of its role in certain solutions. Other possible causes for deviations from the rule are intentionally neglected.

[1] F. Trouton, Phil. Mag. [5] **18**, 54 (1884).
[2] W. Nernst, Göttingen Nachrichten (1906).
[3] E. C. Bingham, J. Am. Chem. Soc. **28**, 723 (1906).
[4] Forcrand, Comptes rendus **156**, 1439, 1648, 1809 (1913).
[5] J. H. Hildebrand, J. Am. Chem. Soc. **37**, 970 (1915); **40**, 45 (1918); cf. *Solubility* (Reinhold Publishing Corporation 1936), pp. 101–103. (There is a numerical error in $\Delta H'$ for benzene.)
[6] Cf. O. K. Rice, J. Chem. Phys. **5**, 353 (1937); R. Newton and H. Eyring, Trans. Faraday Soc. **33**, 73, 80 (1936); H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937); J. E. Lennard Jones, Proc. Roy. Soc. London **A165**, 1 (1938).
[7] J. H. Hildebrand, J. Am. Chem. Soc. **59**, 794 (1937); J. Phys. Chem. **43**, 113 (1939); E. A. Guggenheim, Trans. Faraday Soc. **33**, 151 (1937); R. H. Fowler and G. S. Rushbrooke, Trans. Faraday Soc. **33**, 1272 (1937); H. H. Gilman and P. Gross, J. Am. Chem. Soc. **60**, 1525 (1938).

TABLE I. *Excess entropy of vaporization when log Rc = 0.1.*

SUBSTANCE	ΔS	$\Delta S - 20.1$
$C(CH_3)_4$*	20.1	0.0
i-C_5H_{12}	20.2	0.1
n-C_5H_{12}	20.7	0.6
n-C_6H_{14}	21.5	1.4
n-C_7H_{16}	21.5	1.4
n-C_8H_{18}	21.2	1.1
i-C_6H_{14} (di-isopropyl)	20.3	0.2
Hg	20.1	0.0
CCl_4	20.7	0.6
$SiCl_4$†	21.2	1.1
$SnCl_4$	21.8	1.7
$C(NO_2)_4$	22.6	2.5
$CHCl_3$	21.7	1.6
CH_2Cl_2	20.9	0.7
CS_2	20.3	0.2
1-1-$C_2H_4Cl_2$	21.6	1.5
1-2-$C_2H_4Cl_2$	21.5	1.4
1-2-$C_2H_4Br_2$	21.4	1.3
C_6H_6	21.2	1.1
C_6H_{12} (cyclo)	21.1	1.0
$(C_2H_5)_2O$	21.8	1.7
$(CH_3)_2CO$	22.5	2.4
C_2H_5OH	27.0	6.9
CH_3OH	26.5	6.4

* J. C. Aston and G. H. Messerly, J. Am. Chem. Soc. **58**, 2354 (1936).
† K. Kearby, J. Am. Chem. Soc. **58**, 374 (1936).

Table I gives values for the entropy of vaporization per mole at a vapor concentration corresponding to log $Rc = 0.1$, or $c = 0.0202$ moles per liter. These were obtained by plotting log p against log T on a large scale and finding the slope of a chord between points cut by log $Rc = 0$ and 0.2, respectively. The curvature is sufficiently small and uniform to make this more reproducible than drawing tangents exactly at log $Rc = 0.1$.

The data were taken from the *International Critical Tables* except as indicated in the footnotes to the table.

Tetramethyl methane, neopentane, was selected as a liquid that should have a minimum of structure and consequently also of increase in entropy on vaporization. The third column of the table gives the excess of each entropy of vaporization over that for neopentane, which we may regard as an index of the amount of structure possessed by the liquid in question. A different choice of the standard liquid might affect the absolute magnitudes of this excess entropy but the excellent agreement between neopentane and mercury indicates that such a correction would hardly be significant.

Noteworthy is, first, the marked increase with diminishing symmetry in changing from the neopentane through isopentane to normal pentane; second, the further increase with length of chain beyond normal pentane; the apparent falling off with octane may or may not be real; third, the contrast between normal hexane and its more symmetrical isomer, di-isopropyl.

Turning to the second group of liquids in the table, the value 0.6 for carbon tetrachloride confirms the evidence of slight structure furnished by x-ray diffraction[8] and the further increases with silicon and tin tetrachlorides were to be expected in view of the increasing size of the central atom. The distances from their central atom to the chlorine atom are 1.76, 2.00 and 2.30, respectively.[9] Tetranitro methane offers still more opportunities for distortion and orientation. Carbon disulfide molecules are linear, and some evidence of structure is not unexpected; chloroform and methylene chloride have dipole moment but they are rather compact so it is not strange that they should give evidence of only small orientation.

The evidence for structure in benzene and cyclohexane is particularly interesting in view of the recent findings of Scatchard, Wood and Mochel[10] that these liquids mix with an increase in entropy which is greater than that of a regular solution. Since benzene molecules are flat rings while cyclohexane molecules are puckered rings, it is not strange that their solutions possess less order than each has in the pure state.

The last group is added to show, for comparison, the magnitude of the effect of the other factors. It includes ether, which has a rather large but well buried dipole moment; acetone, with a larger and more exposed dipole, and ethyl alcohol, with a smaller dipole moment than acetone, but showing the much stronger orienting effect of hydrogen bonds, quite in harmony, again, with the evidence of x-ray diffraction.[11]

These findings promise to be rather significant

[8] H. Menke, Physik. Zeits. **33**, 593 (1932).
[9] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **57**, 2684 (1935).
[10] G. Scatchard, S. Wood and J. M. Mochel, J. Phys. Chem. **43**, 119 (1939).
[11] Cf. B. E. Warren, Phys. Rev. **44**, 969 (1933).

in connection with the entropy of solution in two component systems. Thus two normal paraffins may, at least within a certain range, mix without destroying their probably parallel orientation. However, a branched chain hydrocarbon might be expected to diminish the orientation of a straight chain hydrocarbon, with a corresponding increase in the entropy of mixing in excess of $-R(N_1 \ln N_1 + N_2 \ln N_2)$.

There are already several systems that invite this type of treatment. One of the most puzzling, heretofore, has been the solutions of iodine in ethylene bromide which, although violet in color, give solubility curves which are not parallel to those for the other violet solutions, but which deviate in the direction shown by the brown solutions. It would seem, however, that the combination of moment of the C—Br bond with the rotation about the C—C bond, which has been shown to cause variations in the moment of the whole molecule depending on temperature and solvent,[12] offers possibilities of alterations of structure due to changing temperature and iodine content of the solution sufficient to account for the irregular entropy of this solution. Chloroform, on the other hand, which, although having nearly as large a dipole moment as ethylene bromide, has a buried dipole and little possibility of orientation, dissolves iodine to give a solubility curve parallel with those for other violet solutions.

[12] Cf. L. Meyer, Zeits. f. physik. Chemie **B8**, 27 (1930).

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An Absorption Band of Formaldoxime at λ9572*

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The third harmonic of the O—H band in formaldoxime vapor has been found to lie at λ9572 (10,444.1 cm^{-1}) and under high dispersion has been resolved and found to resemble a parallel band of a symmetric rotator. Owing to the weakness of the lines near the center of the band a definitely unique rotational analysis could not be made but the harmonic mean of the two larger moments of inertia appears to lie between the limits 73.3 and 76.6×10^{-40} g cm^2. The hydroxyl hydrogen does not rotate freely and indeed its torsional oscillation appears not to have a very low frequency. It is not possible to locate this hydrogen uniquely until other parameters of the molecule have been determined by electron diffraction. The possible effect of resonance on the O—H frequency is discussed.

EXPERIMENTAL

THE trimer of formaldoxime was prepared in the manner recommended by Scholl.[1] On heating the substance to around 100° it yielded the monomer in the vapor state. The formaldoxime vapor was confined in a ten-foot Pyrex absorption tube at about 100° and one atmosphere. Exploratory spectrograms were first taken with a glass spectograph of moderate dispersion to locate the O—H band. In the resolution of the rotational structure a 21-ft. grating was employed which has a dispersion of about 2.5A per mm in the first order. Eastman 144Q plates sensitized with ammonia were used and the wave-length calibration was made by means of iron lines in the third order.

EXPERIMENTAL RESULTS

As may be seen in Fig. 1, a single O—H band was found at λ9572 (10,444.1 cm^{-1}) with a simple structure apparently identical with that of a parallel band of a symmetrical molecule. In Table I are given the frequencies of the observed lines. These are the average of two independent sets of measurements. In the case of some of the

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, number 681.

[1] R. Scholl, Berichte **24**, 573 (1891).

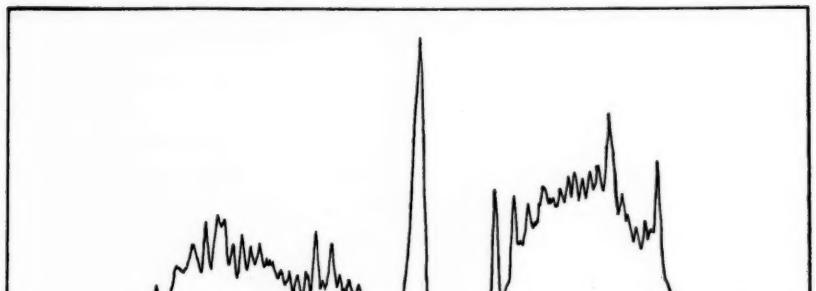

FIG. 1. Microphotometer curve of the O—H band at λ9572 in formaldoxime vapor. The water vapor spectrum in the same region is shown below.

weaker lines the error may be as large as 0.1 cm^{-1}. The separation of the maxima of the P and R branches is 31.0 cm^{-1}.

DISCUSSION OF THE RESULTS

Formaldoxime (H_2CNOH) appears to deviate rather little from being a symmetrical rotator both from considerations regarding its structure and from the appearance of the band here described. Consequently the spacing in this band will, for all practical purposes, be determined by the harmonic mean of the two nearly equal and larger moments of inertia. It should be possible then to evaluate this mean moment of inertia for both upper and lower vibrational states by making the same combinations which would be appropriate for a parallel band.

With the help of a Fortrat diagram J values were assigned to the lines. It was not possible to do this uniquely and in both P and R branches there are two assignments which appear to be equally plausible as shown in Table I. The combinations can consequently be made in four different ways. In obtaining the rotational constants from the combinations $\Delta_2F'(J)=R(J)-P(J)$ and $\Delta_2F(J)=R(J-1)-P(J+1)$, it was found convenient to plot $\Delta_2F''(J)/2(2J+1)$ against $(J+\frac{1}{2})^2$ since the effect of the stretching of the molecule with rotation is quite appreciable, and the extrapolation to the rotationless state would otherwise have been difficult.

The extreme values of the means of the two larger moments of inertia are those given by assignments 1 and 2 of Table I. They are, respectively, as follows: $D''=73.3\times10^{-40}$ and 76.6×10^{-40}, and $D'=73.6\times10^{-40}$ and 76.8×10^{-40}. There is a slight uncertainty in making the extrapolations but it appears very unlikely that the actual values of the moments of inertia should lie much outside the limits given.

TABLE I. *Frequencies of lines in the formaldoxime band at λ9572.*

ν (cm^{-1})	Alternative J Assignments No. 1	No. 2	ν (cm^{-1})	Alternative J Assignments No. 1	No. 2
P branch			*P branch*		
10,411.12	42	43	10,435.66	11	11
11.75	41	42	36.44	10	10
12.49	40	41	37.21	9	9
13.33	39	40	—	—	—
14.13	38	39			
14.91	37	38	*Q branch*		
15.58	36	37			
16.32	35	36	44.13		
17.10	34	35			
17.83	33	34	*R branch*		
18.59	32	33			
19.35	31	32	55.31	15	16
20.13	30	31	56.00	16	17
20.88	29	30	56.64	17	18
—	—	—	57.27	18	19
26.88	22	22	57.92	19	20
27.67	21	21	58.58	20	21
28.46	20	20	59.18	21	22
29.23	19	19	—	—	—
—	—	—	61.41	25	26
31.15	17	17	62.01	26	27
31.86	16	16	62.65	27	28
32.61	15	15	63.28	28	29
33.42	14	14	63.88	29	30
34.21	13	13	—	—	—
—	—	—	66.12	33	34
			66.67	34	35
			67.28	35	36
			67.91	36	37
			68.50	37	38
			69.07	38	39

The Structure of Formaldoxime

Although it is not possible to determine the structure of formaldoxime from the data at present available, some interesting conclusions can be drawn. One of these is quite certain; the others may be somewhat in doubt and await further investigation for their confirmation. The appearance of the band at λ9572 seems to exclude completely the possibility of the free rotation of the hydroxyl hydrogen. The band appears to be simple in structure, and if there are any superposed bands arising from absorption from excited levels they are certainly quite weak. It appears reasonable to conclude that the O−H torsional vibration is not extremely low.

When hydroxyl hydrogen, though not free to rotate, may be found in more than one position of potential minimum, the O−H frequency appears to be considerably different in the different positions unless they correspond to equivalent or very similar configurations of the molecule. The fact that only one O−H band is observed at λ9572 may be taken as indicating that in the great majority of molecules at least the hydroxyl hydrogen is to be found in only one definite position, which one would consequently expect to correspond to a rather deep potential minimum. Since the molecule is most probably planar, it is of interest to speculate as to which of the two geometrically possible plane configurations is the more probable.

In both models the O−H bond makes a considerable angle with the minor axis of the molecule and if the change in electric moment is more or less parallel to this bond it is a little difficult to see how either can give rise to hydroxyl bands so predominantly "parallel" in character as the one observed. However, the one represented in Fig. 2 in which the hydroxyl hydrogen is farthest removed from the carbon atom seems definitely to be more probable.

The moments of inertia of the molecule would be of assistance in locating the hydroxyl hydrogen if the other parameters were known. Some of them can be estimated with sufficient accuracy but since there seems to be some possibility of resonance in formaldoxime one hesitates to make a guess as to the C−N and N−O distances. The latter is particularly uncertain, and the assistance of electron diffraction measurements must be awaited.

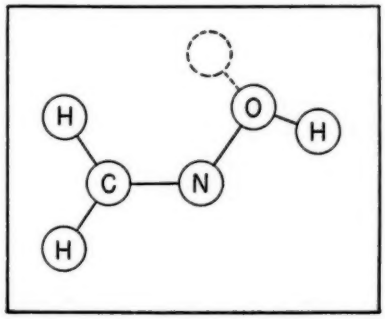

Fig. 2. Possible configurations of the formaldoxime molecule. The less probable location of the hydroxyl hydrogen is shown by dotted lines.

If the N−O bond does have appreciable double bond character, one should expect the O−H frequency to be somewhat affected, probably lowered. An effect of this sort may well be responsible for at least a part of the lowering of the O−H frequency in the carboxylic acids and in nitric acid. Indeed it is possible that the frequency lowering might serve as some measure of the importance of the resonance and it is unfortunate that internuclear distances are not available in any cases which might serve for calibration. However, it is doubtful whether any simple relation exists owing to the presence of numerous other complicating factors.

The third harmonic O−H band of formaldoxime has nearly the same frequency as the analogous one of phenol. In the latter molecule the importance of resonance has already been suggested.[2] In both cases the frequency is indeed slightly lower than in the primary alcohols but may still be regarded as well within the normal range. Consequently it appears unlikely that the N−O and C−O distances in the two molecules, respectively, will be found to be much shorter than the normal single bond distances. Electron diffraction measurements will, however, be awaited with interest.

[2] L. Pauling, J. Am. Chem. Soc. **58**, 94 (1936).

On the Quantum Efficiency of Photosynthesis

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For the maximum quantum efficiency of photosynthesis in green plants, the value $\frac{1}{4}$, which was obtained by Warburg and Negelein, has been generally accepted. However this value has appeared to be less certain since only much smaller efficiencies have been observed in recent experiments employing different methods. Because the theoretical aspect of photosynthesis greatly depends upon the maximum quantum efficiency, it is important that additional experiments be made. As a first step toward the solution of this problem, Warburg and Negelein's experiments have been repeated. When their methods are followed closely, a maximum efficiency of 1/4.2 is observed, which is in good agreement with their value. The remaining question—whether this method actually gives the over-all efficiency for the assimilation of CO_2 under favorable conditions, or merely the efficiency for the reduction of a respiration product intermediate between CO_2 and carbohydrate—is not answered by these experiments. Further experiments along this line are in progress.

I. INTRODUCTION

THE maximum quantum yield for the photoreduction of CO_2 by green plants is a constant of great importance since it strongly conditions any theoretical mechanism set up to explain the photosynthetic process. For many years the value $\frac{1}{4}$, obtained by Warburg and Negelein[1] in their classical experiments, has been generally accepted and made the basis for much theoretical work in this field. However some recently reported experiments on quantum yields,[2] in which methods quite different from those of Warburg and Negelein were used, have resulted in maximum yields considerably less than $\frac{1}{4}$. Furthermore there are reports, unpublished, that repetitions of the original experiment have also failed to give the expected result. Therefore further investigation of the maximum quantum yield for photosynthesis appears to be justified.

It may be worth while to emphasize that the problem involves much more than the performance of accurate chemical and physical measurements. The quantum yield for the photosynthetic process is determined by the following factors: (1) the internal condition of the plant, which may be controlled by methods of culturing and preparation, and (2) the environment of the plant, in which the most important elements are the CO_2 concentration, the intensity of illumination, and the temperature. By "maximum quantum yield" is meant the value obtained when the above factors provide an absolute optimum. A potential criticism of any new measurement, if it results in a value less than $\frac{1}{4}$, is that the above conditions were not so favorable as in the experiments of Warburg and Negelein.

There remains the further question of what interpretation may be attached to a value of the quantum yield obtained in any particular experiment. This question arises because photosynthesis cannot be observed independently of other processes carried on by the plant. Of these, the most important is respiration, which in its external aspects is the exact inverse of photosynthesis—carbohydrates are lost by the plant and O_2 is consumed, with an equivalent production of CO_2. It is generally assumed that during photosynthesis the respiration continues, and that to obtain the actual rate of CO_2 reduction due to photosynthesis, the rate of respiration—which is measured previously or subsequently with the plant in darkness—must be added to the gas exchange observed during illumination. This correction becomes important in experiments on maximum quantum yields, since the yield is highest at low light intensities.

The correction for respiration is especially important in the method of Warburg and Negelein, where thick suspensions of algae are

[1] O. Warburg and E. Negelein, Zeits. f. physik. Chemie **106**, 191 (1923).
[2] W. M. Manning, J. F. Stauffer, O. M. Duggar and F. Daniels, J. Am. Chem. Soc. **60**, 266 (1938).

used to secure total light absorption; the correction is as a rule equal to or greater than the corrected rate of photosynthesis. Because a long period of either illumination or darkness generally results in a changed rate of respiration, Warburg and Negelein used alternate light and dark periods of only ten minutes each. Under these conditions the respiration before and after illumination is the same; thus, presumably, the value during the illumination is known accurately.

The suggestion has been made, however, that the method of Warburg and Negelein does not necessarily give the quantum yield for the reduction of CO_2 and H_2O to carbohydrate and oxygen, for what is observed is not a positive and sustained evolution of oxygen during the illumination, but merely a suppressed or reduced rate of consumption of oxygen for the short period of ten minutes.* One might suppose, for instance, that what occurs is a photochemical splitting off of oxygen from some easily reduced intermediate product of respiration. Against this hypothesis is the fact that an anomaly in the neighborhood of the compensation point has not been discovered in the large number of experiments in which photosynthesis has been studied as a function of light intensity. It is nevertheless desirable that methods be introduced which avoid as far as possible a large correction for respiration, and such experiments are being undertaken by the author. But because of the difficulties which have been encountered by the previous introductions of new methods, and because no independent confirmation of Warburg and Negelein's result has as yet been published, a repetition of their experiments was undertaken first and is to be described in the present paper.

II. Apparatus and Procedure

The apparatus and methods were in principal the same as those used by Warburg and Negelein; generally departures were made only to the extent necessary to adapt the experiments to the equipment available. Those interested in the finer details of the experiments must consult the original papers; the following brief description is intended only to give some degree of completeness to the present paper and to record, where it seems important, variations from the original experiments.

* The reference here is to a lecture given by Emerson at the symposium on photochemistry at Stanford University, August, 1938.

A. Algal suspensions

The plant material consisted of suspensions of unicellular green algae. The method of culture was similar to that described by Warburg and Negelein, with additional precautions to maintain pure cultures.** For most of the experiments the algae were centrifuged from the culture solution and then put into suspension in fresh Knop solution, as in the experiments of Warburg and Negelein. In a few cases 0.02 $M \cdot KHCO_3$ was used instead of Knop solution. The suspensions were saturated with five percent CO_2 in air, which was also used to fill the free volume of the flask. One experiment was performed with algae suspended in a buffer of composition 0.015 $M \cdot K_2CO_3$ $+0.085\ M \cdot KHCO_3$, to which no CO_2 was added; the buffer alone provides a CO_2 concentration of 8×10^{-5} mole/l, which corresponds to 0.15 percent CO_2 in air. All of the experiments were performed at 10°C.

B. Manometric measurements

The exchange of CO_2 and O_2 was measured with a Barcroft differential manometer, which is a U manometer with each end connected to an otherwise closed flask. In use, the flasks are

** The strain of alga was obtained from Dr. Dean Burk of the Fixed Nitrogen Laboratory; it had originally been isolated in New England and identified as *Chlorella pyrenoidosa* by Dr. Florence Meier of the Smithsonian Institution. The culture medium was Knop solution of the following composition:

$MgSO_4$	0.02 M
KNO_3	0.025 M
KH_2PO_4	0.018 M
$FeSO_4$	0.00001 M
$Ca(NO_3)_2$	0.0025 M.

The culture flasks were gas washing bottles blown from ½ l Erlenmeyers; it was found convenient to add at the side of the flask a ground joint through which inoculations could be made or cultures withdrawn by a pipette. Flasks containing 250–300 cc of culture solution were inoculated from a stock culture which was kept in a refrigerator. They were then placed about 20 cm from a 100-watt lamp surrounded by a water bath. The number of cells then doubled in approximately each 12 hours. When a culture had developed a bright green color it was moved to 30 cm from the lamp and the growth continued for three days, when it was used for an experiment. When centrifuged, the total volume of cells from such a culture was about 0.35 cc. Throughout the growth period a gas mixture of 5 percent CO_2 in air was bubbled through the suspension and the illumination was continued during 24 hours per day.

immersed in a constant temperature bath. One flask contains a suspension of algae and the other an equal volume of solution without algae. To obtain measurable pressure changes when CO_2

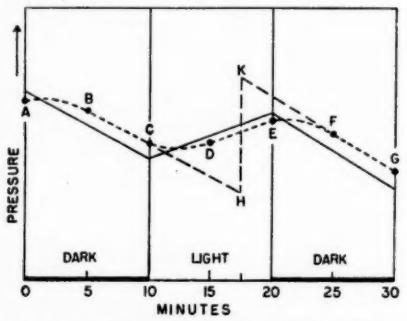

FIG. 1. Relation between photosynthesis and manometer readings. The solid lines represent the assumed course of photosynthesis and respiration. The dotted curve illustrates the pressure changes as read from the manometer.

and O_2 are exchanged in equivalent amounts, the solution in which the algae are suspended must either be a buffer which maintains a constant partial pressure of CO_2 or it must have a volume large enough nearly to fill the flask. In the latter case pressure changes occur because of the very different solubilities of CO_2 and O_2 in water. High concentrations of CO_2 require the use of the latter method. The cross section of the manometer capillary was 0.0036 cm^2, the volume of the flasks 37.6 cm^3 and the manometric fluid was 95 percent ethyl alcohol. With 25 cc of suspension, at 10°C the photosynthesis of 2.22 cubic millimeters of CO_2 to 2.22 cmm O_2 then produces a pressure change of 1 mm alcohol. Throughout the experiments, except for ten seconds at each pressure reading, the flasks are agitated to maintain the equilibrium between dissolved and undissolved gases.*

In spite of the agitation of the flasks, the slowness of the gas exchange between the algal suspension and the free volume in the flask is a potential source of error which can be avoided only by additional precautions. The manometer responds only to changes in the total pressure of the gases in the free space, while the direct effect of respiration and photosynthesis is to change the concentrations of O_2 and CO_2 dissolved in the suspension. A dynamic equilibrium is eventually reached in which the rates of exchange between liquid and free space correspond to the exchanges between algae and liquid; but if the latter rates are suddenly changed by starting or stopping the illumination, the equilibrium is upset and the new equilibrium is established only after some time. The phenomenon is illustrated in Fig. 1, where the solid lines represent the pressure changes as they would occur if the gas exchanges were instantaneous and the dotted curve the changes as actually indicated by the manometer. A case has been represented in which the photosynthesis more than compensates the respiration; otherwise it is typical of the experiments. It is obvious that measurements on the curved portions of the dotted curve should be avoided.

Warburg and Negelein used the following procedure for all of their measurements. With alternate ten-minute periods of light and dark, measurements were made at the points B, C, F, G of Fig. 1. By a computation equivalent to the construction of the broken lines, HK was obtained as the photosynthesis, corrected for respiration, for the entire ten minutes of illumination. In the present experiments exactly the above method was used in many measurements of the quantum yield, but for a check somewhat varied procedures were also tried. In a few cases the illumination was continued for only five minutes, with ten-minute dark periods; in other cases additional pressure readings were generally taken at D and E and the corrected photosynthesis for five minutes computed from $(p_E-p_D)+\frac{1}{2}(p_B-p_C)+\frac{1}{2}(p_F-p_G)$. The lengths of the intervals were also varied; AB, CD and EF ranged from 5 to 10 min. and BC, DE and FG from 5 to 15 min.

C. Photometry

Monochromatic light was produced by a Westinghouse H-3 mercury lamp and filters. By a lens and mirror a monochromatic image of a condensing lens was projected on the bottom of

* It was found that proper shaking was very important if reproducible measurements were to be obtained; a reciprocating motion with an amplitude of 4 mm and frequency of 240/min. was eventually found to be satisfactory. By means of small bits of paper placed in one of the flasks it could be observed that under the above conditions the contents of the flask took up a circular motion, traveling around the flask nearly twice a second. With greater amplitudes the contents splashed about and eventually stopped up the capillary leading to the manometer. At higher frequencies the circular motion was erratic in starting; the papers usually executed only a small oscillation at the bottom of the flask. After these tests the shaking was very carefully regulated and the consistency of the results was much improved.

the reaction flask; the image was about 3.5 cm in diameter—just small enough to fall entirely within the flask when the latter was being shaken. The top and sides of the flask were silvered outside to prevent the escape of light. Measurements showed that with the quantity of cells used (0.3 cc) at most a few percent of the incident light reescaped from the flask; it was therefore necessary to measure only the total light flux in the incident beam to obtain the absorbed energy.

The incident flux was measured with a photoelectric cell within an integrating box, illustrated in Fig. 2. The box could be partially immersed in the water bath to receive the light beam where it normally entered the flask. (Nevertheless a correction for reflected light must be applied.) Comparisons were made for each run with values observed outside the bath so that subsequent intensity measurements could be made during the course of an experiment without disturbing the manometer. The integrating box was calibrated against a small radiation thermocouple which was in turn calibrated with a standard carbon lamp obtained from the National Bureau of Standards. For calibration, the window of the box was placed behind a diaphragm uniformly illuminated with monochromatic light; from the area of the diaphragm and the intensity of illumination—measured in ergs/cm² sec. by the thermocouple—the sensitivity of the box and cell in ergs/sec. could be found. The advantage of the integrating box is that it provides a large uniformly sensitive surface, so that the total flux in a non-uniform beam can be obtained from a single measurement; it is also much less expensive than a large surface thermopile. The disadvantage is that the sensitivity is different for each wave-length and the calibration must be repeated frequently.

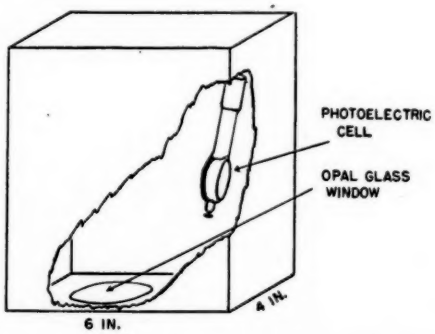

FIG. 2. Integrating box used with photoelectric cell. The walls are coated inside with flat white paint of high reflecting power.

TABLE I. *Wave-length 5780A. Flux = 27.6 × 10⁸ Einsteins/min. Intensity = approximately 1.0 × 10³ ergs/cm² Manometer constant = 2.22 mm³ O_2 at N.T.P./mm alcohol.**

TIME	LIGHT	MANOMETER MM ALCOHOL	Δp
0 min.	off		
5		108.1	
10		103.8	−4.3 mm
10	on		
15		101.8	
20		100.6	−1.2
20	off		
25		97.6	
30		93.6	−4.0

* Computations

Method A

respiration for 15 min. −12.45 mm
$p_{25} - p_{10}$ − 6.2
corrected photosynthesis for 10 min. 6.25
rate of photosynthesis = 1.39 mm³/min. = 6.2×10^{-8} mole/min.
quantum yield = 0.225 = 1/4.5

Method B

respiration for 5 min. −4.15 mm
$p_{20} - p_{15}$ −1.2
corrected photosynthesis for 5 min. 2.95
rate of photosynthesis = 1.31 mm³/min. = 5.8×10^{-8} mole/min.
quantum yield = 0.210 = 1/4.8

TABLE II. (*Experiment 4.*) *Knop solution.*

λ	FLUX × 10⁸ EINSTEINS/MIN.	TOTAL PERIOD OF ILLUMINATION	1/QY METHOD A	AV.	1/QY METHOD B	AV.
5780	45	15	5.2		5.8	
			5.0		5.3	
			5.0	5.05	4.7	5.25
			5.0		5.2	
5780	45	10	4.5		5.5	
			5.0		5.0	
			5.2	4.92	5.5	5.25
			5.0		5.0	
5461	48	10	4.7		5.4	
			5.0	4.87	5.7	5.43
			4.9		5.2	
5461	82	10	5.6		6.5	
			5.7	5.67	6.2	6.10
			5.6		5.6	

III. RESULTS AND DISCUSSION

Quantum yields have been determined from the manometric measurements by the two methods described in Section II*B*. "Method *A*" is that used by Warburg and Negelein; it gives a value of the quantum yield which is an average

TABLE III. (*Experiment 8.*)

λ	FLUX × 10^8 EINSTEINS/MIN.	LIGHT PERIOD	1/*QY* METHOD A	AV.	1/*QY* METHOD B	AV.	SUSPENSION SOLUTION
5780	46	10	4.5		5.1		Knop
			4.7		5.1		
	28.7		4.5	4.56	4.8	4.82	
			4.8		4.6		
		15	4.3		4.5		
5461	31.7	15	4.9		5.3		
	55		5.1	4.83	5.8	5.23	
	21.0		4.5		4.6		
5461	30.8	15	5.1		5.6		0.02*M*·$KHCO_3$
5780	26.3	15	4.5		4.7		

TABLE IV. (*Experiment 9.*)

λ	FLUX × 10^8 EINSTEINS/MIN.	LIGHT PERIOD	1/*QY* METHOD A	AV.	1/*QY* METHOD B	AV.	SUSPENSION SOLUTION
5780	44	10	4.5		5.4		Knop
			4.5		4.8		
		15	6.4	4.98	5.4	5.10	
			5.0		5.1		
	26.7		4.5		4.8		
	44	10	8.2		8.2		0.015*M*·K_2CO_3
			7.9	7.83	8.1	8.17	+0.085*M*·$KHCO_3$
			7.4		8.2		

for the entire period of illumination. "Method *B*" depends upon a rate measurement during the latter part of the illumination period. A typical example of the measurements and the two methods of computation is given in Table I. Series of measurements are shown in Tables II, III and IV; each series was obtained from a different culture of algae.

The photosynthesis for ten minutes, expressed as a pressure difference, amounts to only a few mm. Since each value of the quantum yield depends upon three observed pressure differences, it is not surprising that individual values, obtained on the same algae and under identical conditions, should show fluctuations. (Some of the measurements which were made at the beginning of a run or immediately after an adjustment of the manometer gave inconsistent respiration rates. If the respiration before and after illumination varied by more than ten percent, the quantum yield for that illumination period was excluded.) To obtain a reasonably accurate quantum yield which is characteristic of the suspension of algae working under optimum conditions, averages of several values must be taken. Since these averages should represent the quantum yield for optimum conditions, values were not included in the averages if they were obtained under obviously unfavorable conditions. The only values so excluded are those obtained with a light flux greater than 60 Einsteins per minute and those obtained with the carbonate-bicarbonate buffer. Averages for the last ten experiments performed are given in Table V.*

It is perhaps of some interest that the substitution of 1/50 *M*·$KHCO_3$ for Knop solution as the medium in which the algae were suspended had no observable effects on the quantum efficiencies. This result is shown by the last two

* An estimate of the accuracy of the final results is somewhat arbitrary. The calibration of the standard lamp obtained from the National Bureau of Standards is reported to be in error by not more than 1 percent. The readings on which the energy measurements were based could be made with a comparable accuracy, and there is no apparent reason why the errors in the energy values should be as great as 5 percent. The most likely source of a systematic error in the manometric measurements is inadequacy in the rate of gas exchange; this type of error would be expected to make the observed quantum efficiencies smaller than the actual ones. The accidental errors in the individual measurements of quantum yields are of the order of 10 percent but the probable errors of the averages are of course smaller.

lines of Table I and by the last line of Table V. With the carbonate-bicarbonate buffer, however, the quantum efficiency was reduced 40 percent. According to the published curves relating photosynthesis to CO_2 concentration, one should not expect that this buffer, which produces a CO_2 concentration of 8×10^{-5} mole/l would limit the rate of photosynthesis at low light intensities. It is not improbable that some other property of the buffer—such as a high *p*H—is responsible for the effect.

The results which should be compared with those of Warburg and Negelein are those which were obtained by Method *A*, since it is the method which they used. Their average for eighteen measurements made with the yellow mercury line was 1/4.3. The average of the values in the first column of Table V is 4.8. However, both in the series of values obtained by Warburg and Negelein and in the first column of Table V there is a spread of about 20 percent between the maximum and minimum. These variations appear to be considerably greater than the random experimental error and are therefore attributed to differences in the internal condition of the algae. With this justification, one may assume that the maximum average value of quantum yield for one culture, rather than the average over all cultures, best represents the efficiency for optimum internal conditions. On this basis the maximum quantum yield with yellow light, according to the present experiments, is 1/4.22. This value is the average of six measurements made with the same algal suspension; the internal consistency is represented by a probable error of ±0.14. For the maximum quantum yield with yellow light, the final result is then

$$1/QY=4.22\pm0.14.$$

The eighteen values listed by Warburg are individual measurements, not averages. Of these, the six greatest efficiencies correspond to the numbers 3.8, 3.9, 4.1, 4.1, 4.2 and 4.3.

The quantum efficiencies observed with the green mercury line are systematically lower than for the yellow—in the average, about ten percent. Although the absorption at 5461 is relatively weak, tests by Warburg and Negelein and by the author indicate that the loss of light from the flask is not more than a few percent. However, it is not entirely certain that in the case of the weakly absorbed green light the chlorophyl is altogether responsible for the absorption. Warburg and Negelein regarded their result obtained with green light to be of inferior accuracy. They performed only one experiment with green light—which they term an "orienting experiment"—and omitted the result from their final list of quantum efficiencies. The data which they give for the experiment leads to an efficiency of 1/4.9 for the green and 1/4.4 for the yellow.

No attempt has been made here to repeat Warburg and Negelein's measurements with red and with blue light. The results presented seem to be adequate proof that with proper care their experiments can be repeated with substantially the same results. Additional effort along this line did not appear to be justified, since the more important problem is to follow up experimentally the criticisms of the method mentioned in Section I.

In the foregoing comparison with the results obtained in the original experiments of Warburg and Negelein, the discussion was confined to the quantum efficiencies obtained by Method *A*, since this method was used exclusively in their experiments. Otherwise there is no obvious reason why one method should be preferred over the other. Table V shows that quantum efficiencies obtained by method *B* are consistently lower; the average difference is ten percent. The cause of this minor discrepancy is in doubt. One must conclude either that there is an obscure systematic error in one method of measurement, or that

TABLE V.*

	Method A		Method B	
Experiment	5780	5461	5780	5461
1	4.22	4.96	4.78	5.65
2	5.00	5.64	5.32	6.04
3	4.65		4.78	
4	4.98	4.87	5.25	5.43
5	4.76		4.88	
6	5.05	5.8	5.43	6.2
7	5.55	5.8	5.98	6.0
8	4.55	4.90	4.80	5.32
9	4.98		5.10	
10	4.3		5.0	
Average	4.80	5.33	5.13	5.77

*All experiments performed with Knop solution except Exp. 10 and two measurements of Exp. 8 (Table III); in these cases 0.02 *M* $\cdot KHCO_3$ was used.

under the conditions of these experiments, photosynthesis and respiration do not follow the simple course represented by the solid line in Fig. 1.* It is hoped that experiments now being undertaken will make clearer the cause of the discrepancy.

The experiments reported above were performed in the Physics Laboratory of Johns Hopkins University, and are a part of a larger program under the direction of Professor J. Franck. The writer wishes to express his appreciation to Professor Franck and to the others who have contributed materially to the research. Professor B. Livingston very kindly made available the facilities of the Plant Physiology Department. Professor H. Pfund contributed valuable advice concerning the energy measurements and provided a thermocouple of his own construction. Dr. Dean Burk of the Fixed Nitrogen Laboratory has been a most helpful consultant on the biological aspects of the problem.

* The type of induction period which has been observed for many plants would lead to an effect opposite to that described here. According to Warburg's experiments (reference 3), chlorella does not exhibit an induction period at low light intensities. However, in higher plants, induction periods have recently been shown to occur at light intensities which are low, although not so low as those used in experiments on quantum efficiencies (references 4 and 5).

[3] O. Warburg, Biochem. Zeits. **103**, 188 (1920).

[4] E. D. McAllister, Smithsonian Miscellaneous Collections, **95**, No. 24 (1937).

[5] E. Smith, J. Gen. Physiology **21**, 151 (1937).

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"Surface Elasticity" of Protein Films. I. Egg Albumin*

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The limiting area is the quantity by which protein films are usually described. This may give some indication of the "spreading tendency" of the protein, but it is not necessarily related to other mechanical properties of the film, since an unknown proportion of the protein may remain unspread, or may pass into solution in the substrate. This is demonstrated by an experimental study of the limiting areas and the surface elasticities, $M_S = -A \cdot dF/dA$, of egg albumin films as a function of pH. It is shown that the $M_S - F$ curves for this protein are of characteristic form, with a single well-defined maximum, $(M_S)_{max}$. It is shown further that the characteristic large variations of limiting area with pH are not reflected in the variation of $(M_S)_{max}$ and it is concluded that throughout the range of H ion concentrations studied the observed elasticities are due to a monomolecular film of true limiting area ~1.0 m²/mg. The lower values of the apparent limiting area obtained at certain hydrogen ion concentrations are due principally to unspread material which does not contribute significantly to the mechanical properties of the film. It is suggested that the $M_S - F$ curves should be employed in place of the apparent limiting areas in the description of protein films and that the values of $(M_S)_{max}$ may provide a convenient means of showing specific differences between films of different proteins.

INTRODUCTION

IT is well known that an organic substance insoluble in water but containing a suitable proportion of polar groups can be caused to form a thin layer at an air-water interface. The effect of such layers upon the interfacial tension has been extensively studied in relation to the area covered by a given quantity of the substance, and convergent lines of evidence suggest that over a wide range of interfacial tensions and areas the films may be homogeneous and one molecule in thickness, varying only in the mode of packing of the nonpolar heads and in the orientation of the polar groups with respect to the surface.

In the correlation of force-area (force = lowering of interfacial tension) relations with the structure and orientation of organic molecules it has been customary to make considerable use of "limiting areas" obtained by extrapolating por-

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† Commonwealth Fund Fellow.

tions of the force-area curves to zero pressure, a procedure that is fully justified by the evident relationship of such a quantity to the molecular dimensions of the substance constituting the film. Such limiting areas have indeed proved of value in elucidating the structure of substances of unknown constitution. There are, however, certain obvious circumstances under which the use of limiting areas in the characterization of films could be misleading. Such, for example, would be partial solubility of the substance in the substrate, failure of an undetermined fraction to spread to form an homogeneous film, dilution of the substance added with unknown amounts of other materials, or indefiniteness of molecular weight or particle size. Naturally "limiting areas" obtained from the study of such films will be of little value for descriptive purposes and of less value for the estimation of molecular quantities.

All of these considerations apply to the proteins. These substances may, as a rule, be spread either from the solid or from solution. The film appears to be insoluble in water, but a certain variable fraction of the material added probably enters the substrate during the spreading process and may or may not be adsorbed subsequently at the surface. A further portion may remain unspread, either lying in discrete masses upon the surface of the homogeneous film, or, possibly, forming some sort of micellar network which might influence the mechanical properties of the film. In either case, the computed "limiting area" would have little meaning and might be expected to depend on the particular method of spreading employed. Again, under some conditions the process of spreading may be so slow that there is no certainty that the "limiting area" finally attained relates to the material originally spread rather than to a product of some slow chemical transformation. Thus the limiting area of a protein film is an arbitrary quantity which under the most favorable circumstances may be connected with the so-called "spreading tendency" of the material but which has no necessary connection with the properties of the film itself. It is unfortunate that protein films are usually described solely by their limiting areas, while the force-area curves from which these values are derived are not recorded.

The problem, then, is to find a new means of characterization of protein films in terms of some quantity which can be derived from the force-area diagrams, which is independent of the actual area per milligram or per molecule of protein spread, and which is sufficiently sensitive to be of value in detecting specific differences between proteins or between films of the same protein when spread upon different substrates. As a quantity satisfying the first criterion we have chosen $-A \cdot dF/dA$ which may be called the "surface elasticity," M_S, since the above definition is in conformity with that given by Quincke[1] (1870), who first used the term, and by Schütt,[2] who first investigated the elastic properties of protein films. Plotting M_S against F for several different proteins, we obtained curves which differed reproducibly from one another and which encouraged us to believe that the second criterion also might be satisfied by M_S. At this stage, however, it appeared necessary to make a careful preliminary study of these curves for a single well-defined protein, and of their variation with time of spreading, amount of material spread, and *p*H. For this purpose we chose crystalline egg albumin, the "spreadability" of which has been studied in some detail by Gorter,[3] ter Horst[4] and others. It is the purpose of this paper to present the results obtained.[4a]

Experimental

The surface balance, resembling in most particulars that described by Harkins and Myers,[5] was designed by Mr. A. J. Rawson of this Department. The float was of phosphorbronze coated with a thin layer of high melting paraffin wax; leakage past the float was prevented in some experiments by thin waxed-silk threads, in others by gold ribbons 0.00068 mm thick, rendered more flexible by vertical corrugations and fixed in position with Wood's metal. All other surfaces in contact with the film or the

[1] G. Quincke, Pogg. Ann. **105**, 1 (1858); **139**, 1 (1870). Quoted by Schütt, reference 2.

[2] K. Schütt, Ann. d. Physik (4) **13**, 712–746 (1904).

[3] E. Gorter, Am. J. Dis. Children **47**, 945–956 (1934); Article in C. L. A. Schmidt's *Chemistry of the Proteins and Amino-Acids* (Thomas, Springfield, Illinois, 1938), p. 442.

[4] M. G. ter Horst, Rec. trav. chim. Pays-Bas **55**, 33–42 (1936).

[4a] J. B. Bateman, Cold Spring Harbor Symposium on Quantitative Biology, p. 148 (1938).

[5] W. D. Harkins and R. J. Myers, J. Chem. Phys. **4**, 716–724 (1936).

underlying solution were of chromium-plated brass conditioned with a rubbed-down film of ferric stearate prepared as described by Langmuir and Schaefer.[6] The dimensions of the tray were 25.5×76.3×1 cm.

The water used was obtained from a tin-lined still and collected in a glass carboy. Chemicals used in making up buffer solutions were of reagent quality. With the exception of those of *p*H 1.0, buffers were made up to a total concentration of 0.01 *M* and their *p*H measured with a Beckmann glass electrode. The following solutions were used.

*p*H 1.0	0.1 *M* HCl
2	0.01 *M* HCl
4.7	acetic acid-sodium acetate
6–9	$Na_2HPO_4-KH_2PO_4$
11	Na_2HPO_4-KOH

The final experiments were made with a specimen of crystalline egg albumin prepared by Sörensen's method by Chambers and Flosdorf and stored in lyophil form since 1933. In other experiments a crude commercial preparation (Merck) was used. The solid protein was kept in a microweighing bottle (Pregl "pig") which was weighed on a Sartorius microbalance (for the loan of which we are indebted to the Department of Bacteriology) in order to determine the amount of material transferred to the surface. The latter operation was performed with a platinum loop, the protein being added in small amounts until a pressure of about 0.3 dyne/cm was obtained. The surface was then increased by one-third and left for 15–60 minutes, according to the rate of spreading at the particular *p*H used. The first compression curve was taken in all cases before spreading was complete, but at a time when it was sufficiently slow to be inappreciable over the duration of the measurement. The average time required for a single complete compression was 13 minutes. The curves obtained upon expansion were sometimes recorded, but since in all cases the film showed considerable hysteresis the presentation of these curves will be deferred. This hysteresis, although rarely mentioned in the literature, appears to be a fairly constant property of protein films which requires investigation. All measurements were made at room temperature (23–25°C).

[6] I. Langmuir and V. J. Schaefer, J. Am. Chem. Soc. 59, 2400–2414 (1937).

General Character of Surface Elasticity Curves

The force-area curves which were used as a starting point in the determination of M_S were of the general character of those described by Gorter (1934). These consist of a low pressure region, in which the curve is convex towards the A axis, followed by a transition, usually around $F=6$ dynes/cm, to a high pressure region in which F increases more or less linearly, tending to flatten off gradually above $F=19$. Above $F\sim25$ this decrease in slope becomes much more marked and is accompanied by irreversible changes in the film. It is thus obvious that the curve differs in the high pressure region from the curve of constant surface elasticity, $F=-\ln A$, and measurement shows that this is also the case in the low pressure region. Within the limits of experimental error, $M_S=0$ when $F=0$.* The low pressure portion is represented by a rapid increase of M_S with increasing pressure, reaching a maximum in the neighborhood of the transition to the high pressure region. The maximum is followed by an almost linear decrease, the extent of which depends upon the extent of the linear portion of the $F-A$ curve, and this by a more rapid decrease which continues beyond the limit of reversible compression ($F\sim25$ dynes/cm) (see

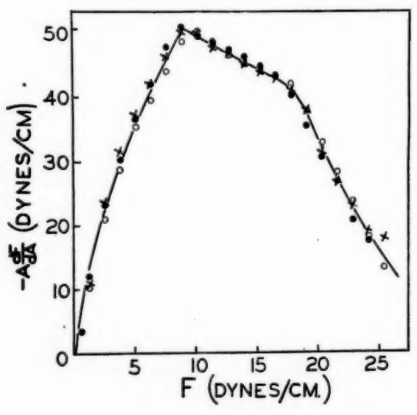


FIG. 1. Force-elasticity curves for egg albumin on 0.01 *M* phosphate buffer, *p*H 7. (● 60 minutes, ○ 120 minutes, × 180 minutes after spreading.) Averaged data from three experiments. Force in dynes cm^{-1}, elasticity in dynes cm^{-1}.

* Since egg albumin forms a coherent film, this statement is untrue without the qualification concerning experimental error, which is too great to permit an exact determination of M_S when $F=0$.

Fig. 1). In the experiments described here, while recording the complete curves whenever necessary, we have given most attention to variations in the maximum value of M, $(M_S)_{max}$, and the corresponding values of F, F_{max}, since these data are convenient for descriptive purposes and must also be of some physical significance.

Relation of M_S to Other Moduli of Elasticity

M_S is an empirical modulus suitable for describing the behavior of a two-dimensional body to which a constraint is applied to prevent any change of dimensions normal to the applied force. It is related to the two-dimensional bulk modulus, K_S, and the two-dimensional modulus of rigidity, N_S, by the equation $M_S = K_S + N_S$. Its relation to the three-dimensional moduli can only be estimated by assuming the film to be isotropic and of mechanically definable thickness z. In this case, $M = zY/(1-\sigma^2)$, where Y is Young's modulus and σ is Poisson's ratio. If $M_S = 50$, $z = 10$A, and $\sigma = 0.5$, then $Y = 3.75 \cdot 10^8$ dynes/cm^2, which is about 100 times greater than the value for 45 percent gelatin estimated from the data of Leick[7] and Sheppard and Sweet.[8]

Effect of Time on M_S

In a number of experiments at different *p*H values the first measurements were made as soon as further increases in force had become negligible over a period of about five minutes, and other measurements were made at intervals of about one hour, the film being left in the expanded state in the intervening period. For three hours after spreading, there is usually a tendency for $(M_S)_{max}$ to decrease by two to five percent. This decrease, however, cannot be attributed wholly to the direct effect of prolonged contact with the substrate, since it is dependent rather upon the change in limiting area (A_0) than upon time. In those occasional cases where the increase of A_0 during the three-hour period was large, the decrease in $(M_S)_{max}$ was also larger than usual, and there was a consistent tendency for the decrease in $(M_S)_{max}$ to increase with the percentage change in A_0. The same tendency appeared when A_0 was increased by removing half of the film from the surface and allowing the remaining portion to expand. In one such case this caused A_0 to increase by 40 percent, while $(M_S)_{max}$ decreased by 7.7 percent. The data show that when A_0 is constant there is an average decrease in $(M_S)_{max}$ of about three percent per hour during the first three hours, while an additional decrease of about 3.5 percent is caused by a ten percent increase in A_0. In a single film which was left for six hours A_0 increased by 18 percent and $(M_S)_{max}$ decreased by only nine percent. The comparatively slight importance of these variations is illustrated in Fig. 1, which shows the curves obtained at 60, 120 and 180 minutes after spreading a film at *p*H 7.0. Nevertheless we considered it advisable when recording the effects of other factors to make measurement within one hour of spreading.

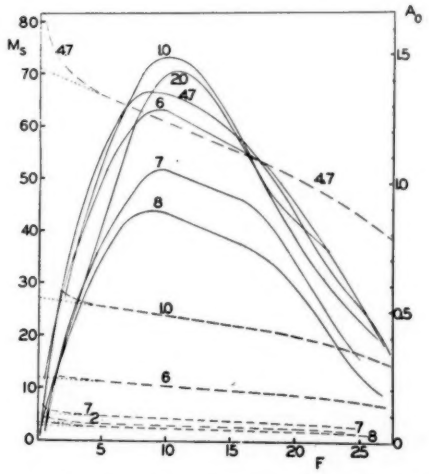


Fig. 2. Force-area (broken lines) and force-elasticity (continuous lines) curves for egg albumin. Numbers attached to each curve give *p*H of substrate; total concentration 0.01 M except at *p*H 1.0, for which substrate was 0.1 M HCl. Force in dynes cm^{-1}, elasticity in dynes cm^{-1}, area in apparent m^2 mg^{-1}, determined from weight of solid protein transferred to surface.

F_{max} is usually 8–9 dynes/cm, but the values in individual experiments are scattered over a range of about ± 1.5 dynes/cm, without any consistent trend in relation to time or limiting area. The wide scatter may be attributed largely to variations in the manner of drawing $F-A$ curves through the experimental points.

[7] A. Leick, Ann. d. Physik (4) **14**, 1939–1952 (1904).
[8] S. E. Sheppard and S. S. Sweet, J. Am. Chem. Soc. **43**, 539–547 (1931).

Effect of *p*H on A_0 and on $(M_S)_{max}$

The present measurements of the limiting area are in broad agreement with those of other workers (Gorter and Philippi,[9] ter Horst[4] and Seastone[10]), showing a sharp maximum in the neighborhood of the isoelectric point of about 1.45 m²/mg, and falling off on both the alkaline and the acid side (Fig. 3, curve 3) to about one-tenth of this value, again rising rather sharply below *p*H 2 and also showing an appreciable rise at *p*H 11.7, the highest used in these experiments. Over the same range F_{max} shows small irregular variations (Fig. 3, curve 2), while $(M_S)_{max}$ (Fig. 2; Fig. 3, curve 1) shows a slow rise on the acid side and a steep decline on the alkaline side of the isoelectric point. The position of the isoelectric point is not made apparent by any uniqueness in the value of $(M_S)_{max}$ at this point, nor does this curve resemble in any way the curve of limiting areas. In Fig. 2 this contrast between the regular variation of $(M_S)_{max}$ and the disproportionate changes in the weight of protein required to form a film of given area at different *p*H values is clearly illustrated by the presentation in the same diagram of the M_S-F curves and the $F-A$ curves from which they were derived. In this diagram changes in the character of the curves with *p*H also become apparent, the "plateau" corresponding to the linear portion of the $F-A$ curves being practically absent at *p*H 1 and 2, and becoming more pronounced with more alkaline substrates.

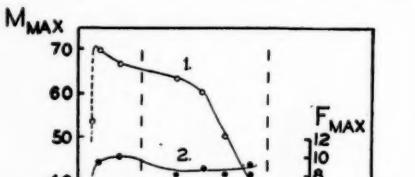


FIG. 3. $(M_S)_{max}$ (top curve), $(F)_{max}$, (middle curve) and apparent limiting areas (bottom curve) as function of *p*H. Units as previously. Vertical broken lines mark boundaries of *p*H stability region as given by Svedberg (J. Am. Chem. Soc. **52**, 2855–2863 (1930)).

Effect of Varying the *p*H of the Solution Beneath a Preformed Film

The foregoing results show that the films formed at various hydrogen ion concentrations are closely similar in their mechanical properties, differing only in the proportion of the protein added that is able to spread in a monolayer; it is almost inconceivable that, if the actual quantities of protein in a homogeneous film showed tenfold variation at different hydrogen ion concentrations, the surface elasticities should vary by only a few percent. A critical test of this conclusion was made in the following manner: a film was spread at the isoelectric point (4.55), a compression curve taken, and the *p*H of the underlying solution then changed to about 2.0. This was accomplished by means of narrow Pyrex tubes running the length of the Langmuir trough and provided with small holes through which the necessary volume of 0.4 *M* HCl could be passed. The solution could then be stirred by gentle lateral movements of the tubes, and the completeness of mixing checked by *p*H measurements. Three curves were made at *p*H 2.1, the last one after one-half of the film had been scraped from the surface. The *p*H of the substrate was then changed to 0.65 by a further addition of HCl, and the measurement repeated. The results are summarized in Table I, together with the results of a second experiment

TABLE I. *Effect of p*H *change on preformed films of egg albumin.*

Expt.	*p*H	Weight of protein in surface (mg)	A_0 (m²/mg)	$(M_S)_{max}$ (dynes/cm)	Time after spreading (minutes)
1.	4.74	0.150	1.07	62.1	13
	2.1	0.150	1.13	62.1	43
	2.1	0.150	1.11	66.9	54
	2.1	0.075	1.15	62.8	64
	0.65	0.075	1.51	39.0	114
2.	4.68	0.122	1.08	60.5	14
	2.05	0.122	1.07	64.0	39
3.	4.83	0.172	0.796	66.6	15
	10	0.172	0.895	56.3	40

[9] E. Gorter and G. T. Philippi, Proc. Kon. Akad. Wet. Amsterdam **37**, 788–793 (1934).
[10] C. V. Seastone, J. Gen. Physiol. **21**, 621–629 (1938).

of the same kind. In a third experiment the substrate was made more alkaline by the addition of a solution containing KOH and Na_2HPO_4; the results of this change are likewise given in Table I.

Discussion

It follows from a comparison of the data given in Fig. 3, with those in Table I that, to a first approximation at least, there is a 1−1 correspondence between the elasticities of an egg albumin film and the *p*H of the substrate at the time of measurement, irrespective of the conditions under which the film was originally formed. Approximately the same variations of $(M_S)_{max}$ with *p*H is apparent whether the measurement is made upon a film spread at the *p*H in question or at some other *p*H. The resemblance extends even to other details in the shape of the M_S-F curves, such as the length of the linear portion. It is evident that throughout the *p*H range the mechanical properties are those of films of which the limiting area is about 1.0 m^2/mg, with comparatively insignificant variations. From this point of view smaller apparent values of A_0 are to be regarded as experimental artifacts, referable to the failure of a certain proportion of the added protein to form a monolayer. We shall not discuss at length the reason for this inability to spread; it may be due to inactivation of the unspread portion, as is suggested by the failure of a significant increase in A_0 to occur even when such films are left in the expanded state or when the *p*H is changed to a value more favorable to the spreading of the original protein (Seastone[10]). It may, on the other hand, be caused by the presence of discrete clumps of unspread material lying on the upper surface of the monolayer, as the observed optical (Zocher and Stiebel[11]) and electrical (Gorter and Philippi[9]) heterogeneity of the film indicates. The surface elasticities also show clearly that the unspread fraction does not contribute markedly to the mechanical behavior of the film, although some slight effect may be discerned in the tendency of $(M_S)_{max}$ to decrease as spreading becomes more complete.

In discussing the form of the elasticity curves and the physical significance of $(M_S)_{max}$, it is convenient to refer to the view, supported by several workers and put forward in its most recent form by Mitchell,[12] that compression of the most highly expanded film is accompanied by a rotation of the polypeptide chain in such a manner that the polar side chains, initially lying

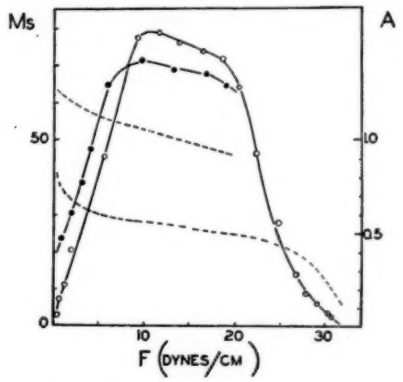


Fig. 4. Force-area (broken lines) and force-elasticity (continuous lines) curves for α-aminostearic acid at *p*H 9.0 (circles and lower force-area curve) and the tripeptide of α-aminocaprylic acid (solid points; *p*H not specified). Elasticities calculated from force-area curves of Porter (1937) and Gorter (1938), respectively. Units as before.

in the plane of the water surface, approach a limiting position in which they are normal both to the axis of the main chain and to the surface, while the nonpolar side chains are in a similar manner removed from the surface, forming a hydrophobic upper surface to the film (Hughes and Rideal[13]). Mitchell identifies the completion of this process with the transition between the low pressure and high pressure regions, and it is reasonable to assume that the value of $(M_S)_{max}$ provides a more exact indication of the transition point. X-ray studies and observations of the birefringence of multilayers of egg albumin deposited from compressed monolayers (Astbury, Bell, Gorter and van Ormondt[14]) confirm the belief implicit in the hypothesis outlined that the polypeptide chains are arranged in parallel rows transverse to the direction of compression. Accordingly the observed compressibilities in the

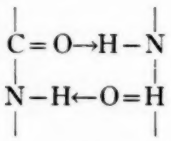
[11] H. Zocher and F. Stiebel, Zeits f. physik Chemie **A147**, 401–435 (1930).

[12] J. S. Mitchell, Trans. Faraday Soc. **33**, 1129–1139 (1937).

[13] A. H. Hughes and E. K. Rideal, Proc. Roy. Soc. **A137**, 62–77 (1932).

[14] W. T. Astbury, F. O. Bell, E. Gorter and J. van Ormondt, Nature **142**, 33 (1938).

high pressure region must be the resultant of the several forces involved in closer packing of polypeptide chains and their accompanying side chains—the attraction or repulsion of polar groups, interaction of the main chains and of the nonpolar side chains, and possibly the dehydration and plication of the main chains. That these forces result in a rapid reversible decrease in elasticity indicates that with the completion of reorientation of side chains cohesive forces between adjoining groups become predominant and may lead upon further compression to the thread formation observed by Devaux[15] (see also Mathieu[16]). Mitchell considers that coordinated hydrogen linkages between the main chains



may occur, and some support for this view may be drawn from the infra-red absorption spectra of dry and hydrated gelatin (Ellis and Bath[17]). However, the dependence of $(M_S)_{max}$ on *p*H might suggest rather that the ionizable groups are chiefly responsible for the increase in compressibility, although it is then difficult to account for the absence of a minimum value of $(M_S)_{max}$ at the isoelectric point, where the lateral adhesion should be much increased by the equal distribution of positive and negative charges.

Both α-aminostearic acid on the alkaline side of the isoelectric point (Porter[18]) and the tripeptide of α-aminocaprylic acid (Gorter, 1938; *p*H unspecified) give surface elasticity curves resembling those of egg albumin (Fig. 4). In these cases also the detailed interpretation of the results is obscure, but they at least make it evident that simpler substances of known constitution can show the same general behavior as the proteins. We consider it undesirable therefore at this stage to discuss the elasticity of protein films in terms of particular hypotheses as to protein structure or in relation to particular phenomena, such as hydration and gelation, which are more or less specific to the proteins.

The discussion of the facts presented in this paper in connection with the study of biological phenomena is of interest in view of the current belief that the properties of living systems are very largely the properties of interfaces. The observed effects of *p*H change on surface elasticity suggest that small environmental *p*H changes are unlikely to produce such radical changes in the properties of membranes as a consideration of the curves of "spreading tendency" might have suggested. To the extent that biological membranes are fixed or "preformed" structures, their stability over a wide range of *p*H can be readily understood; to the extent, on the contrary, that biochemical processes are dependent upon a constant interchange of labile or surface-active materials between plasma and interface, or between homogeneous solution and micelle, we may expect relatively violent effects of environmental change, analogous to the striking variations of spreading tendency which are observed when proteins are brought into contact with different aqueous solutions.

[15] H. Devaux, Bull. soc. francaise de phys. No. 406, 84–85 (1937).
[16] M. Mathieu, Cold Spring Harbor Symposium on Quantitative Biology, p. 186–7 (1938).
[17] J. W. Ellis and J. Bath, J. Chem. Phys. **6**, 723–729 (1938).
[18] E. F. Porter, J. Am. Chem. Soc. **59**, 1883–1888 (1937).

The Symmetry Number and Thermodynamic Functions for Molecules Having Double Minimum Vibrations

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(Received January 12, 1939)

The energy levels and thermodynamic functions for a double minimum vibrational degree of freedom are presented, and their application illustrated for the case of ammonia. A simple formula is given for the range of validity of the classical expressions for rotational heat capacity and entropy. Also the symmetry number, which is troublesome in examples of double minimum vibration, is discussed briefly.

IN CALCULATING thermodynamic functions for gases through the use of molecular structure data it is usual to classify the various degrees of freedom as translational, rotational or vibrational in nature. Furthermore, in approximate treatments one assumes the rotation to be that of a rigid body and the vibration to be harmonic. In treating ethane it was necessary to consider also a restricted rotational degree of freedom, i.e., a system whose motion at low energies is vibration about one or more positions of minimum potential energy, while at higher energies becomes perturbed rotation. The writer has, in fact, prepared tables for the contribution of such a degree of freedom to the various thermodynamic functions and has made several applications.[1]

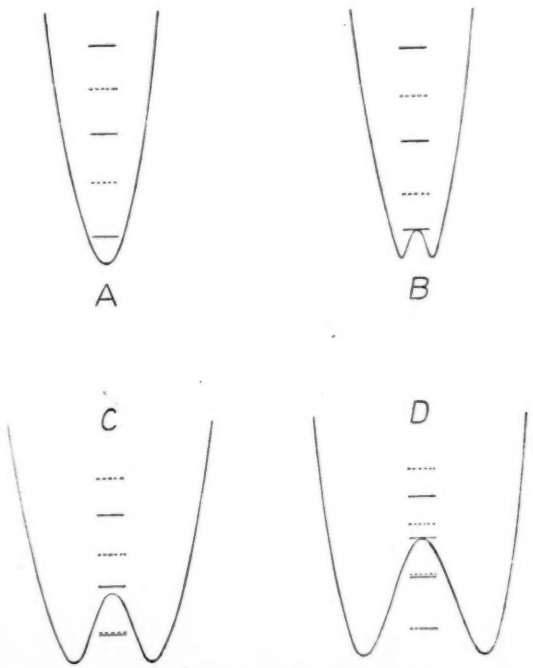

FIG. 1. Four typical potential curves and the corresponding energy levels. Dotted energy levels have antisymmetrical wave functions; solid energy levels have symmetrical wave functions.

Another type of motion which appears in some molecules is a double minimum vibration. The best known example of this motion is found in ammonia, where, although the molecule tends to be pyramidal, the nitrogen can pass through the plane of the three hydrogens without too great an increase in potential energy. In this paper the thermodynamic functions associated with such a motion are discussed. Since the presence of this type of motion is likely to lead to complications in the symmetry number, this aspect is considered briefly. Also a simple expression is set up for a temperature, above which the classical calculations of rotational entropy and heat capacity are satisfactory.

ENERGY LEVELS FOR THE DOUBLE MINIMUM VIBRATOR

The quantum mechanical problem of the symmetrical double minimum vibration has been discussed by a number of authors, who have made various assumptions for the mathematical expression of the potential. The treatment of Manning[2] (who gives references to earlier work) is fundamentally by far the most satisfactory, its only weakness being the fact that the energy levels appear as the roots of a relatively complicated continued fraction. The simple treatment of Wall and Glockler[3] is useful for cases where the central potential barrier is high, while

[1] K. S. Pitzer, J. Chem. Phys. **5**, 469, 473 (1937).
[2] M. F. Manning, J. Chem. Phys. **3**, 136 (1935).
[3] F. T. Wall and G. Glockler, J. Chem. Phys. **5**, 314 (1937).

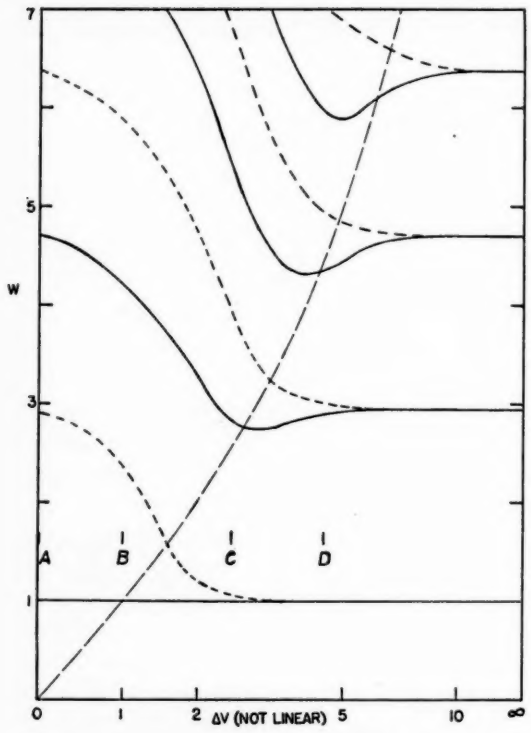

FIG. 2. The energy levels of the double minimum oscillator as a function of the height of intervening potential barrier, DV (dashed line rising to the right). The symmetries of the corresponding wave functions are indicated as in Fig. 1 (dotted = antisym.; solid = sym.). Energy scale is purely for comparison with later figures. A, B, C and D locate the examples in Fig. 1.

for low barriers the writer made a simple calculation in which an error function was added as a perturbation to the usual parabolic potential energy curve of the harmonic oscillator.

Figure 1 presents several potential curves and the resulting energy levels, while Fig. 2 shows how the energy levels behave when the central potential peak is gradually raised. On the right side where the separating potential hill is very large, each of the lower energy levels are doubly degenerate and the corresponding wave functions may be described as symmetrical and antisymmetrical linear combinations of the wave functions for vibration about each minimum. (If, as in optical isomers, the two positions of minimum potential are physically distinguishable, then wave functions representing vibration about only one minimum will have significance.) In the middle of Fig. 2 the pairs of energy levels have separated, the lower one in each case corresponding to the symmetrical wave function. These symmetries are, of course, maintained to the left side where we have the ordinary single minimum oscillator. Because of the arbitrary nature of the assumed potential functions and the lack of immediate applications other than ammonia, these energy levels have been calculated only approximately and are presented only in the graphs.

THERMODYNAMIC FUNCTIONS FOR THE DOUBLE MINIMUM VIBRATOR

The heat capacity and entropy were calculated for the four examples of Fig. 1 as a function of temperature and are shown in Fig. 3. It is noteworthy that at the higher temperatures the heat capacities of "A" and "D" are the same, but that the latter has a peak at very low temperatures. This peak gives "D" an entropy R ln 2 greater than "A" at ordinary temperatures, a fact which will be associated below with the different symmetry numbers ordinarily assigned the corre-

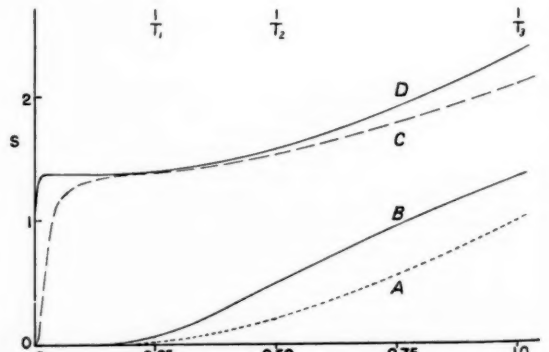

FIG. 3. The heat capacity and entropy in cal. per deg. as a function of temperature for the four systems in Fig. 1. The units of kT are the same as of W in Fig. 2.

sponding molecules. The heat capacity and entropy curves for "*B*" and "*C*" differ from those of harmonic oscillators ("*A*" or "*D*"), however, the entropies always increase in the order "*A*," "*B*," "*C*," "*D*."

Figure 4 shows the entropy for three temperatures as a function of the central potential peak (same scale as in Fig. 2). It is apparent that the entropy increases gradually and continuously from left to right, the difference between the two extremes being $R \ln 2$.

Energy Levels and Thermodynamic Functions for the Entire Molecule

Thus far we have considered the isolated double minimum vibrational degree of freedom; now we must fit these results into the picture of a whole molecule. Two general methods will be considered: first, the exact treatment, setting up the complete wave functions of acceptable symmetry; and second, the modified classical treatment of rotation using the symmetry number.[4]

Taking ammonia as an example, one finds that Hund[5] and Wilson[6] have worked out the various acceptable products of the spin, vibration, rotation, translation and electronic wave functions. There are eight spin functions (for the hydrogens) which fall into two groups of four each, designated by Wilson[6] as $4A$ and $2E$ (the symbol E representing a double degeneracy). Fig. 5 shows first the rotational energy levels of the symmetrical top using the moments of inertia for ammonia. The second and third columns show the acceptable energy levels for the $4A$ and $2E$ groups of spin functions. The dotted lines represent states in which the double minimum vibration wave function is antisymmetric, and which have a slightly higher energy as shown. The usual quantum numbers are indicated on the left side of the diagram and the degeneracies on the right side of each column. The calculation of thermodynamic functions is straight forward, although possibly laborious, once these energy level data are available.[7]

[4] It is assumed that the motion in this degree of freedom can be separated from all others. This will not be the case for a triatomic, almost linear molecule, in which one moment of inertia goes to zero as the molecule vibrates through the linear configuration.

[5] F. Hund, Zeits. f. Physik **43**, 788, 805 (1927).

[6] E. B. Wilson, J. Chem. Phys. **3**, 276 (1935).

[7] W. F. Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

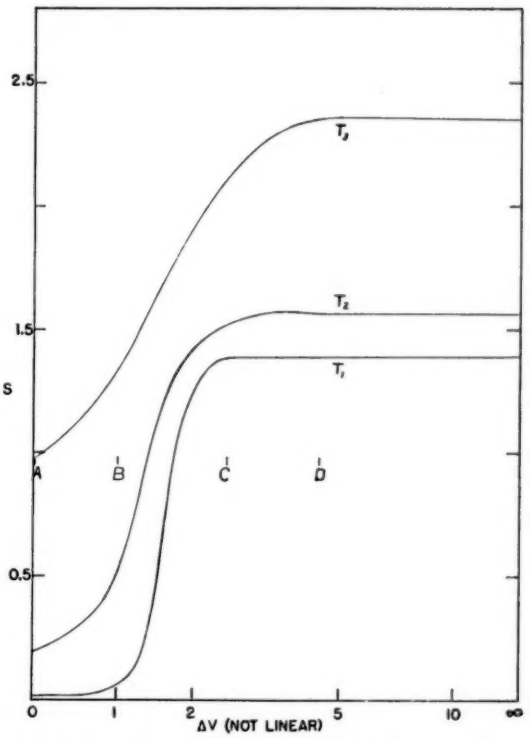

Fig. 4. The entropy of a double minimum oscillator as a function of the intervening potential barrier for the three temperatures indicated on Fig. 3. The abscissa scale is the same as Fig. 2.

At sufficiently high temperatures the effects due to the finite separation of energy levels disappear and the treatment can be correspondingly simplified. The temperature at which this simplification becomes possible varies with the type of motion, and as a result hybrid treatments are usually used. Specifically, translation can, almost without exception, be treated classically (with the usual modification of weight $1/h$ for a unit volume of phase space). Vibration, on the contrary must usually be treated by quantum methods at all ordinary temperatures. It is in the case of rotation that both methods are commonly used. An example of a detailed quantum treatment has been given above, which will now be compared with the classical method.

The formulas for rotational entropy are readily available and need not be repeated here.[8] The rotational heat capacity in the classical treatment is, of course, $\frac{1}{2}R$ per degree of freedom.

[8] (a) L. S. Kassel, J. Am. Chem. Soc. **55**, 1351 (1933); Chem. Rev. **18**, 277 (1936); (b) J. E. Mayer, S. Brunauer and M. G. Mayer, J. Am. Chem. Soc. **55**, 37 (1933).

The two difficulties that arise have to do with the symmetry number,[8(b)] which appears in the entropy formula, and the range of validity of this method.

Ordinarily one would assign a symmetry number of three to pyramidal NH_3 or six to a hypothetical planar NH_3 (SO_3 is presumably a real example). However, if the pyramid is rapidly reversing itself the effective symmetry should also be six. Although the question as to how rapid reversing is needed to change the symmetry number would seem troublesome, it turns out to be otherwise.

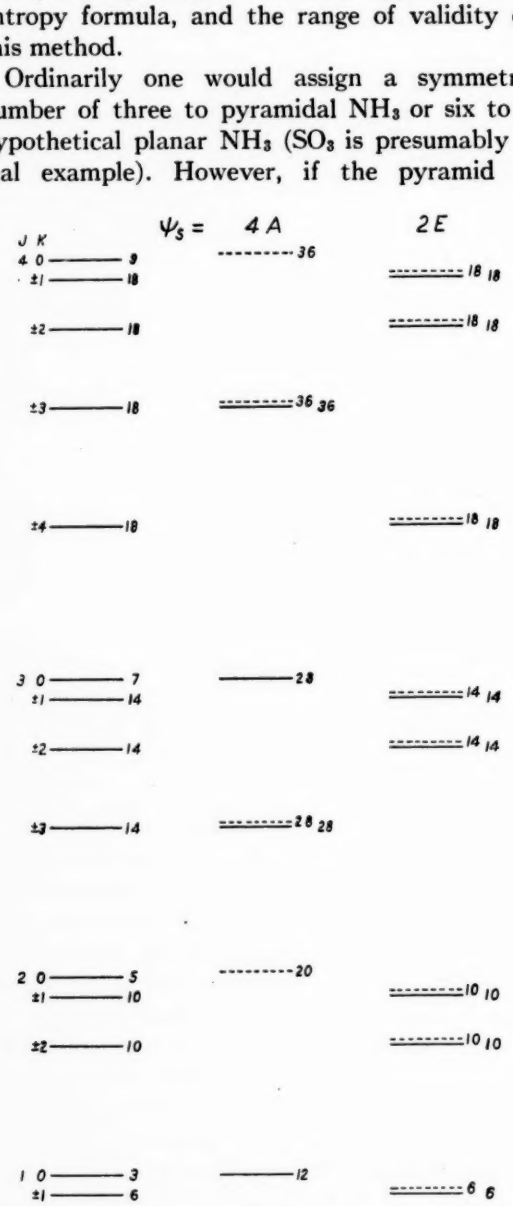

FIG. 5. The rotational energy levels for ammonia. Left column, energy levels for the symmetrical top with moments of inertia for ammonia; middle column, actual energy levels for the four nuclear spin wave functions of symmetry "*A*;" right column, same for two pairs of symmetry "*E*." Numbers on the left are the rotation quantum numbers, on the right of each column, the degeneracies. Dotted lines represent states antisymmetrical to the double minimum vibration, and have slightly higher energies as shown.

Thus one finds that for any height of central potential peak one may consider the possibility of reversal taking the larger symmetry number and the vibration energy levels and thermodynamic functions indicated in Figs. 1, 2, 3 and 4. As an alternate treatment for very high peaks one may neglect the possibility of reversal and take the smaller (half the larger) symmetry number, giving $R \ln 2$ greater rotational entropy, and at the same time take single instead of doubly degenerate vibration energy levels, giving $R \ln 2$ less vibration entropy, or the identical total entropy obtained by the first treatment. The exact, quantum treatment is of course unique and these two methods are to be regarded simply as two equally satisfactory approximations.

It is interesting, moreover, to see how the symmetry number effects enter in Fig. 5. One observes that each of the right-hand columns have 4/3 as many energy levels as the left column, corresponding to the four nuclear spin functions included in each group and the symmetry number of three. If the molecule were planar, all the "dotted" states would be raised to much higher energies and the right-hand columns would have 4/6 as many levels, i.e., a symmetry number of six.

The Use of Thermodynamic Data to Answer Questions Concerning Molecular Structure

The entropy and heat capacity calculations can be reversed in principle and the experimental thermodynamic data used in the determination of molecular structure. A recent example has been the use of the entropy and heat capacity of ethane in the calculation of the height of barrier restricting internal rotation in that molecule. Since the calculation is not readily reversed mathematically, the usual method is to calculate the thermodynamic quantity for all plausible molecular structures and then decide by comparison with the experimental result.

The symmetry of a molecule can frequently be

determined by this method. If all internal motions can be assumed to be harmonic oscillations (single minimum) and their frequencies, together with the mass and moments of inertia are independently known, then these quantities can be substituted in the usual formula and the symmetry number calculated.[9] It seems, however, that this situation will be a rare one. The interpretation of the spectroscopic data usually depends on the assumed structure of the molecule, particularly if the observed values are compared with those calculated from bond force constants. Sometimes a few frequencies are not observed and are known only from such a calculation. The moments of inertia for large molecules are usually calculated from interatomic distances and may or may not depend appreciably on the assumed structure. Also, for example, if one is deciding between a plane or slightly pyramidal $X\,Y_n$ molecule or between a plane or slightly puckered ring, then one must consider the double minimum vibration functions discussed above, since the molecule will be able to "reverse the puckering" without surmounting any very high potential barrier. Thus one finds that the entropy increases continuously as the "puckering" appears and increases.

A completely certain decision on this basis concerning the benzene ring is not possible at present; however, Lord and Andrews[10] have shown that the entropy of benzene agrees with a value calculated by assuming a plane ring and very plausible vibration frequencies.

The Range of Validity of the Classical Formulas

The question of the range of validity of the classical formulas for rotational entropy and heat capacity seems worthy of some discussion. The fundamental test is, of course, a comparison of the result of the exact, quantum calculation with that from the classical formula. From a practical point of view, however, this criterion is as useless as it is safe. One wishes an expression involving only the quantities entering the classical formula, i.e., the temperature, moments of inertia and symmetry number.

The asymptotic expansions given by Kassel[11] and others, in which the first term corresponds to the classical formula, served as a point of departure. The second term in the state sum expansion corresponds to a constant correction to the energy content at the absolute zero and so does not enter the heat capacity or entropy formulas.[12] The third term appears in all functions and may be taken as a criterion of the validity of the classical expressions.

Further consideration, including comparison with the exact calculations now available for a number of molecules, leads to the following as the most convenient expression. If

$$T > T_0 = 1.5 \times 10^{-38} n/I$$

where I is the moment of inertia in g cm^2 and n the symmetry number for rotation about that axis, then the errors in the classical expressions for S and C are less than 0.05 cal. per deg. (Also the errors in expressions for $(H_0^0 - F)/T$ and $H^0 - H_0^0)T$ which include the second term mentioned above are less than 0.05 cal. per deg.) In polyatomic molecules the maximum value of n/I must be used. The error drops rapidly as the temperature increases above T_0 (as $1/T^2$), however, in actual molecules corrections for stretching soon amount to several hundredths of a cal. per degree. The above formula is, of course, unnecessarily severe in some cases, but the differences did not appear sufficient to justify further complications.

To give some specific examples, in methane, I is the same for any axis and is approximately 5.4×10^{-40} while the maximum n for a single axis is 3. One then finds $T_0 = 83°$K. For ethane $T_0 = 42°$K, and for ethylene $T_0 = 53°$K. Further calculations lead to the general conclusion that with the single exception of methane, no organic substance has sufficient vapor pressure for present-day experimental measurements on the gas at temperatures below the limit of validity of the classical formulas for rotational heat capacity and entropy. The closest case (other than methane) is ethylene where the pressure at T_0 is 10^{-9} mm of mercury.

[9] V. Dietz and D. H. Andrews, J. Chem. Phys. **1**, 62 (1933) suggested this procedure.

[10] R. C. Lord and D. H. Andrews, J. Phys. Chem. **41**, 149 (1937).

[11] L. S. Kassel, J. Chem. Phys. **1**, 576 (1933).

[12] From a practical point of view this "second term" correction may often be omitted from the free energy and heat content functions, since the error in E_0^0 (or H_0^0) is a constant and does not affect calculations involving data and applications at high temperatures.

Photolysis of Aldehydes and Ketones in the Presence of Iodine Vapor

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(Received January 18, 1939)

The photolysis of acetone and of formaldehyde takes place principally through a free radical mechanism. The primary processes consist in the splitting off of a methyl radical and a hydrogen atom, respectively. The primary process in the photolysis of methyl ethyl ketone also consists in the splitting off of either a methyl or an ethyl radical. The heat of dissociation of the first hydrogen in formaldehyde is shown to be as low as 78 kcal. Approximately 26 kcal. is required to remove the second hydrogen atom.

A PRELIMINARY report of this investigation has been published recently.[1] In addition a paper[2] on the photolysis of acetaldehyde has been presented for publication. Leighton[3] in a recent review article on the photolysis of aldehydes and ketones remarks that one of the present problems in the photochemistry of aldehydes and ketones is the determination of the relative importance of the three primary reactions

$$\text{I. } R_1R_2CO+h\nu\rightarrow R_1R_2+CO$$

$$\text{II. } R_1R_2CO+h\nu\rightarrow R_1+R_2CO$$

$$\text{III. } R_1R_2CO+h\nu\rightarrow R_1+R_2+CO.$$

The purpose of the present investigation was to determine the relative probabilities of these three reactions for the simpler aldehydes and ketones. The method consisted in the quenching of the free radicals primarily formed by iodine vapor to form the corresponding alkyl halides. Saturated hydrocarbons that may be formed by direct splitting from the aldehyde or ketone do not react with iodine in the temperature range investigated. By an analysis of the reaction products, it is thus possible to distinguish quantitatively, primary reactions giving free radicals from those yielding saturated hydrocarbons. The R_2CO radicals were found to be unusually stable, enabling one to distinguish between reactions II and III.

I. ACETONE

The experimental procedure was almost identically the same as that already described in the case of acetaldehyde.[2] Acetone of C.P. grade was purified by recrystallization with sodium iodide. It was further twice fractionally distilled in vacuum at 10°C before admitting into the reaction vessel. The vapor was slowly mixed with iodine vapor, to avoid condensation of the iodine and resultant formation of solid iodo compounds with acetone. In the vapor phase, blank experiments performed up to 150°C, showed no detectable thermal reaction with the iodine. As previously, the quantum yield of the reaction with iodine was determined by comparison with the direct photolysis at 60°C. This was nearly the temperature employed in the experiments of Damon and Daniels[4] on the quantum yields of the acetone photolysis. Their value of 0.17 at high intensities was adopted. (At low intensities they give a value of 0.29 ± 0.06 at 3130 and 0.33 at 2650A. They give no measurements at high intensities at 2650A but we have assumed that since the yields are equal at these two wavelengths for low intensities that it would also be true for high intensities. At any rate this assumption turned out to be self consistent in that the quantum yields measured in this way were nearly unity for both filtered and unfiltered light.) The quantum yield increases at low intensities but none of our measurements were carried out at intensities low enough for this effect to be important. The methods of analysis

* This work was carried out at the Karpov Physico-Chemical Institute in Moscow U.S.S.R.
[1] Acta Physicochimica **8**, 513 (1938).
[2] Acta Physicochimica **9**, 681 (1938).
[3] P. A. Leighton, J. Phys. Chem. **42**, 749 (1938).
[4] G. H. Damon and F. Daniels, J. Am. Chem. Soc. **55**, 2363 (1933).

for CH_3I and CO were the same as described previously in the case of acetaldehyde.[2]

Since the quantum yield, according to Damon and Daniels, is independent of the wave-length, the quantum yield of the reaction with iodine could be determined by direct comparison of the rates in the full light of a mercury arc. The results of these experiments are given in Table I. The first column gives the pressure of acetone vapor reduced to 60°C, the second the initial pressure of iodine in mm, the third the temperature, the fourth and fifth the number of moles times 10^6 of CH_3I and CO formed, the sixth the time of illumination and the seventh gives the quantum yield for the formation of CH_3I. The quantum yield for the formation of CH_3I is thus unity, so that the primary process must be simply

$$CH_3COCH_3+h\nu\rightarrow CH_3+CH_3CO$$

with an efficiency of unity. This conclusion is essentially in agreement with that of Taylor and Rosenblum,[5] who concluded on the basis of experiments on the photolysis in the presence of hydrogen that acetone decomposes principally through a free radical mechanism.

It is also seen that, in the presence of iodine and at temperatures below 80°, only a very slight amount of carbon monoxide is formed. This points to a high stability of the acetyl radical. The stability of the acetyl radical has in fact been demonstrated earlier by the detection of biacetyl among the products of the photolysis at room temperature.[6, 7]

Acetyl iodide was determined in the reaction products by distilling in vacuum over a heated mercury trap to remove the excess iodine and then collecting in a liquid-air trap. The resultant mixture was freed of methyl iodide by distilling off this substance with 80 percent of the acetone at −30°C in vacuum. The residual liquid was treated with water to hydrolyze the acetyl iodide forming hydriodic acid. An analysis for hydriodic acid by oxidation with bromine water to iodate followed by addition of excess iodide to liberate free iodine was then carried out. The results of this analysis are shown in Table II. It is seen that the reaction is incomplete, only from 10–40 percent of the acetyl radicals combining with iodine. The fact that the amount of acetyl iodide formed appears to be roughly proportional to the iodine pressure, would suggest that the incompleteness of this reaction is not due to slowness but to the rapid establishment of the equilibrium.

TABLE I. *Experiments in unfiltered light.*

Exp.	Press. mm Acetone	Press. mm Iodine	Temp. °C	Moles ×10⁶ CH_3I	Moles ×10⁶ CO	Time min.	γCH_3I	Moles ×10⁶ CH_3COI
1	652	4	80	21.4	0.40	30	1.00	
2	652	0	60	—	3.63	30	—	
3	365	2	80	17.6	0.39	30	0.91	
4	365	0	60	—	3.29	30	—	
5	616	1	80	18.7	0.36	30	0.93	2.5
6	616	0	60	—	3.42	30	—	—
7	561	1	60	19.4	0.10	30	0.94	2.2
8	561	0	60	—	3.51	30		

TABLE II. *Experiments in unfiltered light on the stability of the acetyl radical and the formation of acetyl iodide.*

Press. Acetone	Init. Press. Iodine	Moles ×10⁶ CH_3I	Moles ×10⁶ CH_3COI	Moles ×10⁶ CO	Temp. °C
165	4	21.7	9.3	1.62	100
487	2	43.0	4.0	2.67	100
430	4	29.4	8.8	5.28	115
156	2	36.8	4.6	5.82	115
517	4	14.6	7.0	4.96	128
169	2	41.6	3.4	15.02	130

$$CH_3CO+I_2\rightleftarrows CH_3COI+I. \qquad (1)$$

If the rate of recombination of iodine atoms were given by $-dI/t=k_1(I)^2P$, where P is the total pressure, and of acetyl radicals to form biacetyl by $-d(CH_3CO)/dt=k_2(CH_3CO)^2$ then, under the assumption of the above equilibrium, the amount of acetyl iodide formed would be simply proportional to the iodine concentration at the end of the reaction and independent of the extent of the reaction

$$(CH_3COI)_{final}=K\left(\frac{k_1P}{k_2}\right)^{\frac{1}{2}}(I_2)_{final}.$$

K is the equilibrium constant for reaction I. It is seen that there is qualitative agreement between this equation and the experimental results.

No attempt was made to analyze quantitatively for diacetyl, but its presence was demon-

[5] H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1938).
[6] M. Barak and D. W. G. Style, Nature **135**, 307 (1935).
[7] R. Spence and W. Wild, Nature **138**, 206 (1936); J. Chem. Soc. 352 (1937).

strated qualitatively by treating the residual liquid with hydroxylamine hydrochloride and then precipitating the red nickel dimethyl glyoxime salt.

Spence and Wild found that, although a considerable quantity of biacetyl was formed at room temperature, upon raising the temperature to 60°C no trace of biacetyl could be found. From our results, however, it is evident that this is not due to decomposition of the acetyl radical into methyl and carbon monoxide but to the secondary reaction.

$$CH_3+CH_3CO\rightarrow C_2H_6+CO.$$

As a matter of fact, from the amount of carbon monoxide formed (in the presence of I_2) it is evident that even at 100°C only about eight percent of the acetyl radicals decompose before combining to give either acetyl iodide or biacetyl. The amount of carbon monoxide increases with the temperature, however, as shown in Table II. From the temperature coefficient of the carbon monoxide formation, a rough *minimum* value of 17 kilocalories for the energy of activation of the decomposition into methyl radicals and carbon monoxide is deducible.

The results in filtered light of wave-length 3130A are given in Table III. The quantum yield for the formation of methyl iodide is slightly less than unity. This may be due to some inactivation of the excited acetone molecules by collision, since the presence of fluorescence[3, 8] points to a rather long-lived excited molecule. Damon and Daniels[3] give an upper limit of three percent for loss of absorbed energy due to fluorescence. Matheson and Noyes[9] have recently shown that the fluorescent spectra of acetone and biacetyl are identical for wave-lengths longer than 5000A, indicating that acetone itself is not the emitting species. These facts taken together show that the loss of energy due to fluorescence cannot cause an appreciable lowering of the quantum efficiency.

Spence and Wild[7] have proposed, from the fact that the ratio C_2H_6/CO decreases towards unity in filtered light of wave-length 3130A, that, at these wave-lengths, the predominant process might be the direct splitting off of C_2H_6. Our results do not support this conclusion and the primary process at 3130A must remain predominantly $C_2H_6CO+h\nu\rightarrow CH_3+CH_3CO$.

TABLE III. *Experiments in filtered light.* $\lambda=3130$A.

Exp.	Press. Acetone	Press. Iodine mm	Temp. °C	Moles $\times10^6$ CH_3I	Moles $\times10^6$ CO	Time min.	γCH_3I
1	852	1	90	5.67		120	0.85
2	852	0	80	—	1.13	120	—
3	1265	0.5	90	8.76	—	120	0.78
4	1265	0	80	—	1.90	120	

Damon and Daniels[4] report that the quantum yield increases at low intensities. It is difficult to understand this, as, on the basis of the proposed mechanism, there should be no dependence of the quantum yield on the light intensity. The only possibility is that a reaction of the methyl radicals with acetone becomes important at low intensities. However, this reaction if it does occur, cannot set up reaction chains, since Leermakers[10] found that the quantum yield for the photolysis is only slightly greater than unity even at 400°C.

II. Acetaldehyde

This case has been treated in detail elsewhere[2] so that we will content ourselves with a brief recapitulation of the main conclusions reached. Two primary reactions were found to take place

$$CH_3CHO+h\nu \begin{cases} \nearrow CH_4+CO & \text{I} \\ \searrow CH_3+CHO & \text{II} \end{cases}$$

The sum of the quantum yields for both reactions was found to be unity within the experimental error at both wave-lengths studied, $\lambda=3130$A and $\lambda=2536$A. At 3130A reaction II is 2.6 times as probable as reaction I, while at 2536A reaction I is 2.9 times as probable as reaction II. The low quantum yield at $\lambda=3130$A must thus be due to recombination of the free radicals, methyl and formyl, as in the case of acetone. The increased probability of reaction I at lower wave-lengths thus explains the increase

[8] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, J. Chem. Soc. 1456 (1934).
[9] M. S. Matheson and W. A. Noyes, J. Am. Chem. Soc. **60**, 1857 (1938).
[10] J. A. Leermakers, J. Am. Chem. Soc. **56**, 1899 (1934).

in the quantum yield from 0.3 to 0.9 observed by Leighton and Blacet.[11]

The formyl radicals were found to be very stable with respect to the decomposition HCO $\rightarrow$H+CO and reacted mainly to give formaldehyde and CO i.e., HCO+HCO$\rightarrow$$H_2CO$+CO. At temperatures above 100°C the reaction HCO+$I_2$$\rightarrow$HI+I+CO is observed. The temperature coefficient of this reaction gives a minimum value of 26 kcal. for the activation energy for the reaction HCO$\rightarrow$H+CO.

Blacet and Roof[12] have observed an increase in the amount of hydrogen produced at the lower wave-lengths. This has been interpreted[13] as meaning that the free radical mechanism becomes more predominant at 2537A than at 3130A. This is in disagreement with our results. The production of hydrogen at 2537A, however, may possibly be explained by a direct reaction of an energy rich formyl radical with acetaldehyde.

$$HCO^*+CH_3CHO\rightarrow H_2+CO+CH_3CO.$$

No polymerization was found in the presence of iodine, indicating that polymerization is induced by free radicals. The decrease in the amount of polymerization with wave-length again confirms the conclusion that the free radical mechanism becomes less probable at low wave-lengths.

According to Leighton and Blacet[11] the quantum efficiency of the straight photolysis at 3130A increases with increasing intensity. This suggests that, as in the case of acetone, secondary reactions of the free radicals with acetaldehyde take place even at low temperatures. Blacet and Volman,[14] have in fact, recently suggested, to account for this fact, a chain mechanism for the photolysis even at 30°C. The quantum efficiency for the primary process, however, remains unity under all conditions.

III. Formaldehyde

Paraformaldehyde was purified by warming in a stream of dried nitrogen and freezing out in a liquid-air trap. The liquid air was then removed from the trap and the escaping monomeric formaldehyde was repolymerized by impinging upon a cold surface. A weighed amount of this polymer was then introduced into the apparatus. The bulb in which the formaldehyde was placed was first evacuated thoroughly and then, after closing the valve to the pumps, it was heated with an auxiliary furnace to 160°C. The resulting monomeric formaldehyde was then allowed to diffuse slowly, through a magnetically operated glass valve, into the reaction bulb containing a known amount of iodine vapor. The pressure of formaldehyde was calculated from a knowledge of the volume of the system. The quantum yield for the reaction in the presence of iodine was determined, as before, by comparison with the yields for the decomposition in the absence of iodine as reported by Norrish and Kirkbride.[15] They report a quantum yield of 0.7 at 3650A and very close to unity at lower wave-lengths.

The isolation of the lines in the mercury arc around 2500A and around 3100A was carried out as before.[2] In addition experiments were made at 3650A. This line was isolated by a glass filter containing a layer 1 cm in depth of a 0.03 percent solution of diamantfuxin.

After illumination, the remaining free iodine was removed by passing the formaldehyde gas through a trap containing a pool of heated mercury and into a liquid-air trap. The permanent gases were pumped off and analyzed for CO by oxidation over I_2O_5 and for H_2 by combustion with O_2 over a heated platinum wire as described previously.[2] Hydrogen iodide was analyzed by removing the liquid air and allowing the unpolymerized formaldehyde along with the hydrogen iodide to distill into a trap containing a concentrated solution of potassium hydroxide. Part of the formaldehyde, however, invariably polymerized and occluded hydrogen iodide in it. This part was accordingly dissolved in water and added to the part which distilled over into the KOH. It was necessary to introduce a slight modification in the previous method for the analysis of iodide[2] since the presence of formaldehyde interfered with the procedure. After acidifying, the iodide was accordingly precipitated as silver iodide and collected and washed

[11] P. A. Leighton and F. E. Blacet, J. Am. Chem. Soc. **55**, 1766 (1933).
[12] F. E. Blacet and J. G. Roof, J. Am. Chem. Soc. **58**, 278 (1936).
[13] G. K. Rollefson, J. Phys. Chem. **41**, 259 (1937).
[14] F. E. Blacet and D. Volman, J. Am. Chem. Soc. **60**, 1243 (1938).
[15] R. G. W. Norrish and F. W. Kirkbride, J. Chem. Soc. **42**, 1518 (1932).

on a glass filter. The silver iodide was then oxidized to silver bromide and iodate ion by passing successive portions of bromine water through the filter. After removing the excess bromine by steam distillation the iodate was treated with iodide, liberating iodine, which was titrated with standard thiosulfate.

The results are given in Table IV. The first column gives the wave-length, the second the pressure of formaldehyde, the third the pressure of iodine, the fourth, fifth and sixth columns give the number of moles of HI, CO and H_2 times 10^6, respectively. The experiments with and without iodine were always done in pairs so that the seventh column gives the ratio of the rates of formation of carbon monoxide for the experiments in the presence of iodine to the successive experiments in the absence of iodine. The next to the last column gives the ratio of the amount of HI formed to that of CO. The last column gives the quantum yield for the formation of HI.

It is seen that at 3130A and 2537A the permanent gases consist almost exclusively of carbon monoxide, there being only a few percent of hydrogen formed. In addition, the HI/CO ratio is nearly equal to two for all the experiments at these wave-lengths. These facts show that the main reaction is splitting off hydrogen atoms. Since it takes 102 kcal. to pull off the two hydrogen atoms from formaldehyde it is obvious that a quantum of light of wave-length 3130A possesses only sufficient energy to detach one hydrogen atom. The primary process at 3130A must therefore be $H_2CO+h\nu \rightarrow H+HCO$ (I). This, in the presence of iodine, would be followed by

$$H+I_2=HI+I$$

and

$$HCO+HCO=H_2CO+CO.$$

We see that the quantum efficiency for the formation of hydrogen iodide is about unity, and that the rate of formation of CO in the presence of I_2 is about $\frac{1}{2}$ as large as it is in the absence of iodine, as is required by the above mechanism.

At 2537A the primary process

$$H_2CO+h\nu \rightarrow H+H+CO \qquad (II)$$

becomes energetically possible. If this were the case, the quantum efficiency for the formation of HI should become equal to two while

TABLE IV. *Formaldehyde+I_2 at 100°C.*

Wave-Length A	Press. H_2CO mm	Press. I_2 mm	moles $\times 10^6$ HI	moles $\times 10^6$ CO	moles $\times 10^6$ H_2	$\frac{d[CO]_{I_2}}{d[CO]}$	$\frac{HI}{CO}$	γ_{HI}
3130	85	4	12.6	7.0	0.1	0.53	1.8	0.97
3130	88	0	—	13.0	12.5	—	—	
3130	115	2	17.4	9.2	0.1	0.51	1.9	0.96
3130	117	0	—	18.1	17.7	—	—	
3130	215	1	19.3	11.6	0.1	0.61	1.7	0.84
3130	212	0	—	16.2	15.8	—	—	
2537	96	2	11.3	6.5	0.0	0.57	1.7	0.95
2537	96	0	—	11.8	11.9	—	—	—
2537	157	5	21.7	13.0	0.1	0.55	1.7	0.86
2537	154	0	—	25.2	25.0	—	—	—
2537	246	5	8.6	5.2	0.1	0.51	1.65	0.85
2537	247	0		10.1	9.9	—	—	—
						H_2/CO	HI/H_2	
3650	154	3	14.6	13.6	6.3	0.46	2.4	
3650	152	0	—	15.2	15.4	1.00	—	
3650	240	1	9.7	9.1	4.4	0.48	2.2	
3650	239	0	—	12.2	11.6	0.95	—	
Exp. with HgI_2 vapor as acceptor								
3650	175	4	14.8	12.5	5.3	0.42	2.8	
3650	177	0		14.9	14.1	0.95		

$d[CO]_{I_2}/d[CO]$ should now be unity. There is no significant change in the values at 2537A as compared to those at 3130A, so that we may conclude that the primary process remains principally I. A simultaneous occurrence of II to the extent of ten percent is not, however, precluded by our data.

At 3650A a considerable quantity of hydrogen is formed. However hydrogen iodide is formed also and more carbon monoxide is formed than hydrogen. The ratio is about two as was previously the ratio HI/CO. This points therefore to two independent primary processes. The ratio of the probabilities of these two reactions is equal to the HI/H_2 ratio and is as 0.7 is to 0.3. That is, if the sum of the quantum yields of the two reactions is unity, that of I is 0.7 and of II is 0.3. The spectrum

$$H_2CO+h\nu \begin{cases} \nearrow H+HCO & \text{I} \\ \searrow H_2+CO & \text{II} \end{cases}$$

of formaldehyde[16] in this wave-length region exhibits fine structure and consequently the excited molecule must have a relatively long life. It might be objected therefore that we are dealing with a direct reaction between the excited formaldehyde molecule and iodine

$$H_2CO^*+I_2=2HI+CO.$$

This is very unlikely since the quantum yield for

[16] G. H. Dieke and G. B. Kistiakowsky, Proc. Nat. Acad. Sci. **18**, 367 (1932).

the formation of HI is independent of the iodine pressure. In order to show this even more conclusively HgI_2 vapor was substituted for I_2 as an acceptor for H atoms. The ratio of the probabilities for these two reactions was found to be the same as with I_2.

These results lead to a surprisingly small value for the heat of dissociation of the first hydrogen in formaldehyde. A mole quantum of light of wave-length 3650A possesses energy equivalent to 78 kilocalories, consequently the heat of dissociation of the first hydrogen is not greater than 78 kcal. Mecke[17] has identified the predissociation limit in the absorption spectrum with the first dissociation and consequently assigned to it a value of 102 kcal. The predissociation limit, however, can only give an upper limit[18, 19] to the heat of dissociation. Thus in SO_2[20] the predissociation limit corresponds to an energy of 13 kcal. greater than the heat of dissociation into SO and O.

Patat[21] has found that in the photochemical oxidation of formaldehyde the ratio of H_2/CO is greater than unity in the continuum while it is very nearly equal to unity in the banded region. He concluded from this fact that hydrogen atoms are primarily formed in the continuum but not in the banded region. Carruthers and Norrish[22] have shown however that these experiments cannot be used to detect hydrogen atoms since formic acid is the first product of the oxidation, a large portion of the permanent gases being derived from the subsequent photolysis of the formic acid. The reaction was also found to be a chain reaction with a large quantum yield.

Akeroyd and Norrish[23] in studying the chain photolysis of formaldehyde have used a suggestion made previously[24] that the primary process consists in the rapid successive breaking off of the two hydrogen atoms. Our results show, however, that only one hydrogen atom is ejected in the primary process and that, furthermore, the formyl radical is quite stable, about 26 kilocalories being required to dissociate it. This stability of the formyl radical has also been remarked upon by earlier workers.[25, 26] We therefore propose to replace Akeroyd and Norrish's scheme for the chain photolysis by the following one

$$\begin{aligned} H_2CO+h\nu &\rightarrow H+HCO \\ HCO &\rightarrow H+CO & k_1 \\ H+H_2CO &\rightarrow H_2+H+CO & k_2 \\ H+HCO &\rightarrow H_2+CO & k_3 \\ H+H &\rightarrow H_2 & k_4. \end{aligned}$$

This leads to the equation for the steady-state concentration of hydrogen atoms.

$$I_{abs}-\frac{k_y}{2}(H)^2-\frac{k_3k_4}{2k_1}(H)^3=0. \qquad (1)$$

Now, k_1 has a large temperature coefficient corresponding to 26 kilocalories and therefore, at low temperatures, we should expect the second term to be dominant while at high temperatures the third term will be the largest. Thus, in the lower temperature range, the rate should be given approximately by

$$-\frac{d(H_2CO)}{dt}=I_{abs}+k_2\left(\frac{2I_{abs}}{k_4}\right)^{\frac{1}{2}}(H_2CO), \qquad (2)$$

while at higher temperatures the rate would be given by

$$-\frac{d(H_2CO)}{dt}=I_{abs}+k_2\left(\frac{2k_1I_{abs}}{k_3k_4}\right)^{\frac{1}{2}}(H_2CO). \qquad (3)$$

The temperature coefficient at the higher temperatures thus should be considerably greater than at the lower temperatures. This is just what Akeroyd and Norrish found, there being a rather sharp change in the temperature coefficient between 200 and 250°C. Now k_3 should have a small activation energy. If we use five kilocalories for k_3 and the value 26 kcal. found for k_1 then, using the experimental value of 16.2 kcal. for the over-all activation energy of the photolysis at high temperatures, we find a value of 9.2 calories for k_2. This is of the order of magnitude of the

[17] R. Mecke, Zeits. f. Electrochemie **36**, 589 (1930).
[18] G. Herzberg, Zeits. f. Physik **61**, 604 (1930); Zeits. f. physik. Chemie **B10**, 189 (1930).
[19] L. A. Turner, Phys. Rev. **68**, 178 (1931).
[20] J. Franck, H. Sponer and E. Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).
[21] F. Patat, Zeits. f. physik. Chemie **B25**, 208. F. Patat and T. Locker, Zeits. f. physik. Chemie **B27**, 431 (1935).
[22] J. E. Carruthers and R. G. W. Norrish, J. Chem. Soc. 1036 (1936).
[23] E. I. Akeroyd and R. G. W. Norrish, J. Chem. Soc. 890 (1936).
[24] C. H. Bamford and R. G. W. Norrish, J. Chem. Soc. 1504 (1935).
[25] F. Patat, Zeits. f. physik. Chemie **B32**, 274 (1936).
[26] M. Burton, J. Am. Chem. Soc. **60**, 212 (1938).

value 10 kcal. obtained for the similar reaction involving acetaldehyde.[25] Part of the fall in the temperature coefficient must of course be attributed to the constant terms in (2) and (3). The data are not sufficient to correct accurately for this effect, but a rough estimate of the temperature coefficient in the low temperature region, taking this into account gives a value of 6–8 kcal., in fair agreement with the value for k_2 calculated from the high temperature region.

Methyl Ethyl Ketone

Some experiments were also carried out with methyl ethyl ketone in the presence of I_2. Since the quantum yield in the near ultraviolet apparently has not been previously determined, no comparison of the rates in the presence and absence of I_2 was made. A few comparisons were made, however, of the rates of the reactions of iodine with acetone and with methyl ethyl ketone under comparable conditions. In addition to CO some hydrocarbon was formed. The carbon hydrogen ratio of the hydrocarbon was determined in much the same way as previously was done for methane.[2] The analyses for alkyl iodide and carbon monoxide were carried out in the same way as previously. Experiments were carried out both in filtered and unfiltered light. The results are given in Table V.

The gaseous products were collected by means of a high speed diffusion pump after freezing out the ketone in liquid air. The vapor pressure of propane is of the order of 1.5×10^{-3} mm at liquid-air temperatures, but since the diffusion pump pumped down to 10^{-5} mm with a fore vacuum of 0.05 mm, it was fairly certain that all the propane was collected. The pressure of gas collected in the fore-vacuum of the diffusion pump was of the order of 0.05 to 0.1 mm. At any rate, after reducing the fore vacuum to 10^{-5} mm and thawing out and refreezing the ketone, no appreciable quantity of gas was further collected. The analysis of the carbon hydrogen ratio $CnHm$ was not accurate due to the small quantities available for analysis. It corresponded to the value for propane, however, within the limits of experimental error.

We see from the results in Table II that methyl ethyl ketone behaves very much like acetone. The amount of CO formed is very small compared with the amounts of alkyl iodide indicating that the principal primary reaction is either

Table V. *The photolysis of methyl ethyl ketone in the presence of iodine at 70°C.*

Press. MeCOEt mm	Wave-Length	Press. Iodine mm	Moles $\times10^6$ RI	Moles $\times10^6$ CO	Moles $\times10^6$ C_3H_8
65	3130	4	22.2	1.05	.82
70	3130	2	21.2	.89	.74
67	Unfiltered	4	17.2	1.24	1.12
72	Unfiltered	2	17.6	1.33	1.24

Comparison of rates of photolysis of acetone and methyl ethyl ketone in the presence of iodine and unfiltered light.

Press.	Substance	Time	Moles $\times10^6$ RI
90	MeCOEt	40	24.6
90	Acetone	40	21.7
90	MeCOEt	40	22.1
90	Acetone	40	20.6

$$C_2H_5COCH_3 \rightarrow C_2H_5 + CH_3CO \qquad \text{I}$$

or

$$C_2H_5COCH_3 \rightarrow CH_3 + C_2H_5CO. \qquad \text{II}$$

Since no attempt was made to analyze separately for CH_3I and C_2H_5I our results are incapable of distinguishing between the two. As before diketones were detected qualitatively by precipitation as the nickel glyoxime salt. The fact that Norrish and Appleyard[27] found that ethane, propane and butane were formed in equal amounts in the direct photolysis would seem to indicate that I and II have about equal probabilities.

It is to be noted that the amount of CO always exceeds the amount of C_3H_8. This is probably to be attributed to a slight thermal decomposition of the acyl radicals. However a few percent of the type of reaction postulated by Norrish[24, 27] and co-workers cannot be definitely

$$R_1R_2CO + h\nu \rightarrow R_1 + R_2 + CO \qquad \text{III}$$

ruled out. The formation of propane must be explained by the independent primary reaction

$$CH_3COC_2H_5 + h\nu \rightarrow C_3H_8 + CO. \qquad \text{IV}$$

In unfiltered light about 6.5 percent of the ketone decomposes in this way while in filtered light of wave-length 3130A 3.5 percent decomposes in this way.

[27] R. G. W. Norrish and M. E. S. Appleyard, J. Chem. Soc. 874 (1934).

Norrish and Appleyard[27] postulate for the higher ketones a new kind of primary process represented by the reaction

$$C_2H_5COCH_3 \rightarrow CH_2 : CH_2 + CH_3CHO \qquad V$$

in the case of methyl ethyl ketone. Such an over-all reaction could also possibly be explained by a secondary reaction such as

$$C_2H_5 + CH_3CO \rightarrow C_2H_4 + CH_3CHO.$$

If ethylene diiodide were found among the products of the reaction with iodine then it would be good evidence that reaction V occurs in a single step. However, no attempt was made in the present work to detect $C_2H_4I_2$.

In the last three experiments we have compared the rates of the reactions of iodine with MeCOEt and Me_2CO. We see that the MeCOEt reaction is about ten percent faster than the reaction with acetone under the same conditions. The absorption coefficient of MeCOEt in the liquid state[28] averages about 20 percent higher than that of acetone while in alcohol[29] it is about five percent higher. It is probable that it is, therefore, also slightly higher in the vapor phase. We may conclude therefore, that the quantum yield for the primary process is MeCOEt is also about unity and that reaction V postulated by Norrish and Appleyard[27] most likely occurs by secondary processes.*

Recombination of Free Radicals

It is a common characteristic of the photolysis of aldehydes and ketones that though the quantum yield for the primary process is very nearly unity, the net yield at low temperatures is only a fraction of this. As has been shown above, this low yield is due to the recombination of the free radicals primarily produced. The increase in the yield at higher temperatures is due to two factors. The first is the setting in of a chain reaction and the second an increasing probability for the reaction $R_1 + R_2CO \rightarrow R_1R_2 + CO$ in place of their simple recombination. Even in the case of formaldehyde, though the quantum yield is about unity at 100° the lowest temperature measured, the yield of the nonchain part of the reaction is less than unity. This can be shown by fitting the kinetic expression $d(HCHO)/dt = k_1 + k_2(HCHO)$ to the data of Akeroyd and Norrish[28] at 100°C. The constant k_1 corresponds to the nonchain part of the reaction and since it is responsible for about $\frac{1}{2}$ of the over-all reaction at this temperature, the quantum yield for the nonchain part is only about 0.5.

It is easy to show that if we had a system of reactions of the type

$$\begin{aligned} AB + h\nu &\rightarrow A + B \\ A + A &\rightarrow A_2 \qquad k_1 \\ B + B &\rightarrow B_2 \qquad k_2 \\ A + B &\rightarrow AB \qquad k_3 \end{aligned}$$

and that even if the activation energies for all three reactions were zero, that the quantum yield would be only about $\frac{1}{3}$.

If there were no activation energy in the true sense of the word, the two radicals would be attracted to one another by polarization forces. This attractive force will be opposed by the centrifugal force of the rotation of the two free radicals considered as a diatomic rotator. There will thus be a maximum of potential energy at quite a large distance of separation, whose position will depend upon the amount of rotational energy, and which corresponds to the activated complex. The vibrational and rotational degrees of freedom of the free radicals will be relatively unaffected due to their large separation in the activated complex. The problem of their rate of recombination can be treated then as if they were atoms and follows exactly the treatment given for a similar case by Eyring, Hirschfelder and Taylor.[30] This calculation has been given in more detail in (2) and we will simply write down the result for the rate constant

$$k = 3(2)^{1/6} J(\tfrac{2}{3}) \left(\frac{\alpha_A \alpha_B I_A I_B}{I_A + I_B} \right)^{\frac{1}{2}} \times \frac{\pi^{\frac{1}{2}} (kT)^{1/6}}{\sigma_{AB}} \frac{M_A M_B}{(M_A + M_B)^{5/2}}.$$

α_A and α_B are the polarizabilities of radicals A and B, I_A and I_B are the ionization potentials,

[28] Beilecki and Henri, Ber. **45**, 2819 (1912).
[29] Beilecki and Henri, Ber. **46**, 3627 (1913).
* See, however, C. H. Bamford and R. G. W. Norrish, J. Chem. Soc. 1531 (1938).

[30] H. Eyring, J. O. Hirschfelder and H. S. Taylor, J. Chem. Phys. **4**, 479 (1936).

M_A and M_B the masses, and $J(2/3)$ the gamma-function of two-thirds. σ_{AB} is the symmetry number for the two free radicals considered as the diatomic molecule. Now for k_1 and k_2, $\sigma=2$ while for k_3, $\sigma=1$. The rest of this expression does not show much variation for the three reactions. Therefore $k_1 : k_2 : k_3 \sim 1 : 1 : 2$ and the quantum yield.

$$\gamma=\frac{1}{1+k_3(1/k_1k_2)^{\frac{1}{2}}}=\frac{1}{1+2}=\frac{1}{3}.$$

It should be remarked here, that on this basis Norrish and Appleyard[27] should have found a ratio 1 : 4 : 1 of ethane to propane to butane as against their observed value of 1 : 1 : 1, in the products of the photolysis of methyl ethyl ketone, provided that the two free radicals ethyl and methyl were split off simultaneously in the primary process. Our results show, however, that only one radical is split off at a time and that therefore the formation of the hydrocarbons proceeds mainly through reactions of the type $CH_3+C_2H_5CO\rightarrow C_3H_8+CO$ and $CH_3+CH_3CO\rightarrow C_2H_6+CO$ etc. These reactions no doubt would involve small activation energies so that it would be impossible to predict the relative amounts of ethane propane and butane that would be formed. If the formation of a methyl or an ethyl radical in the primary process had equal probability and the above secondary reactions had equal rates then the ratio of ethane to propane to butane should be 1 : 2 : 1.

Bond Energies

From thermochemical data[31] the reaction $HCHO\rightarrow 2H+CO$ is endothermic to the extent of 104 kcal. We have derived above a maximum value of 78 kcal. for the strength of the first bond in formaldehyde and a value of 26 kcal. for the strength of the second bond. It is thus seen that in order for their sum to be equal to 104 kcal. we must identify them with their real values. Previously it had been assumed, on the basis of identifying the predissociation limit in formaldehyde with the strength of the first bond, that nearly all of the 104 kcal. was required to dissociate the first hydrogen and that the second dissociated with great ease.

It is also possible with these values, and the value of 17 kcal. found for the reaction $CH_3CO\rightarrow CH_3+CO$ to deduce a value for the strength of the first bond in methane not inconsistent with other estimates. We assume that it also takes 78 kcal. to remove the aldehyde hydrogen in acetaldehyde. This, of course, is not strictly true, but we should expect that the C−H in acetaldehyde would be within five kcal. of that in formaldehyde. This value combined with the value 17 kcal. for the dissociation of the acetyl radical and the fact that the reaction $CH_3CHO\rightarrow CH_4+CO$ is exothermic to extent of one kcal. gives 96 kcal. for the heat of dissociation of the first hydrogen in methane.

Trenner, Morikawa and Taylor[32] have derived a value of 108 kcal., from the heats of activation that they were able to obtain for the reactions CH_4+D and CH_3+HD. Polanyi and Hartel[33] have deduced an upper limit of 110 kcal. from the fact that chlorine atoms react rapidly with methane. They also give a lower limit of 98 kcal. derived from observations on the reactions CH_3+H_2 and CH_4+H. Because of an uncertainty of possibly as much as five kcal. in thermochemical data for the reaction $CH_3CHO\rightarrow CH_4+CO$ it is possible to bring our value within these limits. It does not seem possible, however, accepting the value 78 kcal. for the heat of dissociation of the first hydrogen in acetaldehyde to obtain a value quite as high as Trenner's.

I wish to express my appreciation to Professors A. Frumkin and A. Rabinowitsch for the hospitality extended to me during my stay at the Karpov Institute.

[31] F. R. Bichowsky and F. D. Rossini, *Thermo Chemistry of Chemical Substances* (1936).

[32] N. R. Trenner, K. Morikawa and H. S. Taylor, J. Chem. Phys. **5**, 203 (1937).

[33] H. v. Hartel and M. Polanyi, Zeits. f. physik. Chemie **11**, 97 (1931).

Optical Sensitizing of Silver Halides by Dyes

I. Adsorption of Sensitizing Dyes*

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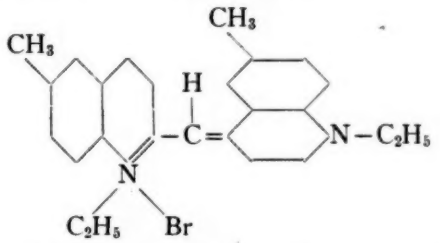
The adsorption of a number of sensitizing dyes to silver bromide has been studied analytically. Basic dyes of the cyanine type are adsorbed completely (irreversibly) from aqueous solutions, but the velocity of adsorption is greatly reduced by the presence of gelatin. Adsorption is oriented, the dye molecules being held by the hydrophile, ionizable side of the molecule, and presenting the hydrophobe portion to the solution, for a primary monolayer; in several cases a second monolayer is formed with the orientation reversed. Calculations of the adsorption-density at saturation (primary monolayer) agree with "edge-on" adsorption of the dye molecules in approximately close-packed assemblages. In agreement with the spectrographic finding of Leermakers, Carroll and Staud, with several of the cyanine dyes, at least two states of aggregation must be assigned to the adsorbed dye. These are provisionally regarded as unimolecular and multimolecular, and show characteristically different absorption and sensitizing bands. Acid dyes, such as erythrosin, which contain nonadsorbed solubilizing (hydrophile) groups are incompletely (reversibly) adsorbed, but also appear to be oriented at the surface similarly to the cyanine dyes.

THE first condition for optical sensitizing by dyes is their adsorption to the solid silver halide. This is a necessary but not a sufficient condition (since certain dyes are adsorbed without sensitizing). It is desirable that the character of this adsorption, in regard to the forces involved, the extent of the adsorption, and its effect upon the adsorbed molecules, be quantitatively determined. The first quantitative studies on this subject were made in 1928[1] by Sheppard and Crouch. They measured the amount of dye removed from a solution and determined the relation between adsorbed dye and the *residual* concentration. This they did in two ways. First, by measuring colorimetrically, or rather, spectrophotometrically, the change in concentration of the dye solution, after shaking up with a silver halide, thus measuring the dye removed as a difference. Secondly, or alternatively, they separated the dyed silver halide centrifugally, dissolved it in thiosulfate solution, extracted it with chloroform, and determined the dye again by spectrophotometric comparison.

They concluded that with dye solutions of increasing concentration a state of saturation of the silver halide surface is reached (a flat or plateau part of the curve) but that this is followed by another (ascending) part of the curve. These authors considered that their results up to the plateau could be represented by an equation deduced by Langmuir[2] for the adsorption of gases in a monomolecular layer.

Assuming that the plateau level represented saturation, they calculated from the integral area of the silver bromide grains used (see below) that with a monomolecular layer of the dye, every dye molecule was "covering" about 3 bromide ions of the crystal surface.

The dye in question, Orthochrome T, is an isocyanine, with the constitution



and is a basic dye, of which the larger part forms the cation D^+, the smaller the anion X^-, where X^- may be Cl^-, Br^-, I^-, $SO_3{-}H$, etc. It was concluded by Sheppard and Crouch that the adsorption consisted effectively in the electrostatic attraction of the dye cation D^+ for an external halide ion of the silver halide crystal. On the other hand, with so-called acid dyes, of

* Communication No. 703 from the Kodak Research Laboratories.

[1] S. E. Sheppard and H. Crouch, J. Phys. Chem. **32**, 751 (1928).

[2] I. Langmuir, J. Am. Chem. Soc. **40**, 1368 (1918).

the type of eosin and erythrosin, we may consider that the dye *anion*, E^-, is held, primarily by electrostatic forces, to a silver cation of a silver halide lattice. Experiments of Sheppard, Lambert, and Keenan[3] on the effects of halide and silver ions, respectively, on the adsorption of these two classes of dyes (basic and acidic) qualitatively confirmed these conceptions.

However, the existence of adsorption isotherms such as those demonstrated by Sheppard and Crouch,[1] if true equilibria, would imply reversibility of the adsorption. Also this is implicit in the application of the Langmuir adsorption theory. This means that the silver halide saturated with the dye from aqueous solution should give up the dye to water. To the contrary Heisenberg[4] found that the adsorption of a dye of this type (carbocyanine) from water was *complete*, and similar results were observed by Leermakers, Carroll and Staud.[5] This contradiction has been cleared up in the present investigation.

Adsorption from Aqueous Solution on Pure Silver Bromide

A hydrosol of pure AgBr was prepared similar to that described by Bokinik and Iljina.[6] This was prepared as follows:

Materials

1. Distilled water	800 cc
2. 0.404 *N* potassium bromide	50 cc
3. 0.400 *N* silver nitrate	50 cc
4. 0.20 *M* sodium bicarbonate	50 cc
5. Water+dye	50 cc

The potassium bromide and silver nitrate were added from pipettes to the distilled water while it was stirring, 50 cc of 0.2 *M* sodium bicarbonate were dumped in from a graduate and, after a moment's stirring, a mixture of 50 cc of dye and water was added. The sol was stirred for 30 minutes to allow the dye to adsorb and then further treatment given as desired. Carbon dioxide was bubbled through the solution during all experiments. This gives a *p*H of 7.6.

Determination of the amount of dye adsorbed to these particles is complicated by the difficulty of separating the colloid phase completely. A partial separation was effected by centrifuging at 1000 r.p.m. for one hour, but a small residuum remained and prevented accurate determination of the amount of dye removed from the solution.* Coagulation of the sol, e.g., by addition of aluminum salts, has the disadvantage that this may also coagulate the dye, so that a true separation is not effected. However, it is possible that a technique of coagulation with silver ions may avoid this, and this is being studied. In any case, after adding a certain amount of basic dye to a given amount of the AgBr sol, coagulation takes place, the solution being cleared of both silver halide and dye. On addition of fresh dye to the supernatant liquid, the coagulum is gradually repeptized and with a sufficient amount, approximately the same as required for coagulation, completely. The evidence here is that both prior to and up to coagulation, the adsorption of the dye is complete, irreversible, and very rapid. The adsorption is apparently to be attributed primarily to the electrostatic attraction of the dye cation D^+ for a halide ion Br^-, etc., of the silver halide lattice. This is supported by the influence of the bromide ion and silver ion concentration, respectively, upon the adsorption. Expressing $-\log [Ag^+]$ as *p*Ag—by analogy with *p*H—the curve in Fig. 1 indicates that above a *p*Ag of 6 the adsorption is practically independ-

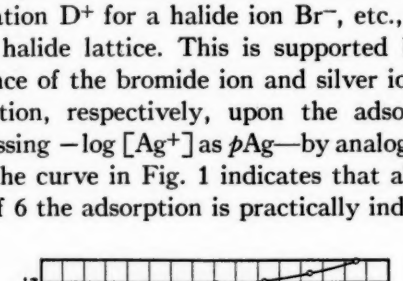


FIG. 1. Effect of *p*Ag on adsorption of dye IVb.

[3] S. E. Sheppard, R. H. Lambert and R. L. Keenan, J. Phys. Chem. **36**, 174 (1932).
[4] E. Heisenberg, Veröff. wiss. Zentr.-Lab. d. phot. Abteil. Agfa **3**, 115 (1933).
[5] J. A. Leermakers, B. H. Carroll and C. J. Staud, J. Chem. Phys. **5**, 878 (1937).
[6] J. I. Bokinik and Z. A. Iljina, Acta Physicochimica **3**, 383 (1935).

* Complete removal was not effected at 35,000 r.p.m., radius 2.5 cm.

ent of bromide ion concentration, but that from *p*Ag 6 down to *p*Ag 3 there is a rapid fall in adsorption, which becomes practically zero for sufficient silver ion covering of the silver halide. This is in agreement with the findings of Leermakers, Carroll and Staud.[5]

The character of the adsorption of the polymethine dyes is not simply explicable in terms of the low solubility of the dye halide D^+X^-, as might be deduced from the various "adsorption rules" of Paneth (Fajans, *et al.*[7]) because the solubility of the dye in water, although small, is finite, yet there is no desorption by water. In effect, the facts are best explained by the assumption of *oriented* adsorption of the dye molecules. In general the molecule has what may be termed a polar (hydrophile) aspect, and a nonpolar (organophile) one. The former is conditioned by the tertiary—*N* atom, or more exactly by the residual (coordination) affinity of the tautomerically equivalent key—nitrogens of the resonance chain for the anion (Cl^-, Br^-, I^-, etc.). One may symbolize such a molecule, as in the simpler case of a fatty acid residue, by ♀, where the circle indicates the organophile portion, the arrowhead the polar or hydrophile portion. Roughly speaking, the solubility of these dyes in water is due to the polar and ionizable part of the molecule, although as noted later this solubility is never very considerable. Alternatively, solubility in organic solvents, more especially in less polar solvents, is due to the cyclic nuclei and their substituents.

The question of "solubility" of these dyes will be discussed more fully in a following paper.

Since the adsorption of the polymethine (cyanine) dyes to polar solids such as the silver halides consists in the fixation of the polar aspect of the molecule to the crystal lattice, this leaves the nonpolar organophile portion exposed to the medium. Evidence will now be presented to show that this fixation continues until the surface of the crystal is covered with these leaf-like molecules piled on edge-wise in as close packing as is compatible with their own possible solid structure *and* with the surface structure of the crystal, to form a "parallel piled, edge-on" monomolecular layer. The new surface of the crystal (or crystallite, for hydrosols) has no hold upon water, so that the adsorption from water is

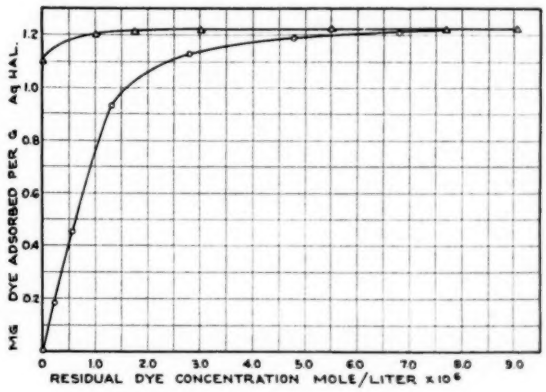


Fig. 2. Adsorption of dye IVb to silver bromide; *p*H = 7.3; 0.5 percent gelatin; temp. = 25°C; o = 2 hr. agitation; Δ = 16 hr. agitation.

complete and irreversible. On the other hand, there is attraction between the organophile parts of these surface-oriented molecules, so that colliding particles (in a sol) aggregate and precipitate, as already noted. This stage corresponds to primary monomolecular saturation of the surface.

The stage of "primary saturation" may be determined for the polymethine dyes in two ways: (a) with a hydrosol of silver halide by titrating with dye solution to the point of coagulation, (b) with a suspension of silver halide grains in gelatin solutions (a photographic emulsion) by shaking with equal volumes of dye solutions of varying concentration until apparent equilibrium is reached, separating the grains centrifugally, and determining either or both the residual dye in the solution, the dye adsorbed to the silver halide grains. The technique used is that developed by Sheppard and Crouch.[1] It consists in extracting the dye with an organic solvent little or slightly miscible with water, and determining the dye spectrophotometrically at an absorption maximum. In the case of silver halide grains, these are first dissolved in sodium thiosulfate solution, from which the dye is then extracted. Sheppard and Crouch used chloroform, but it has been found by E. E. Jelley and

[7] K. Fajans, and K. Von Beckerath, Zeits. f. physik. Chemie **97**, 478 (1921); K. Fajans, *Eder's Handb. d. Photo.* Bd. 2, Part I, third edition, 645 (1927); K. Fajans and T. Erdey-Grúz, Zeits. f. physik. Chemie **A158**, 97 (1931); R. Pohl, Dissertation (Munich, 1924).

B. H. Carroll of these Laboratories* that in most cases a higher partition (practically complete extraction) can be obtained with butyl alcohol. This will be discussed more fully in a later paper dealing with the state in solution of the dyes.

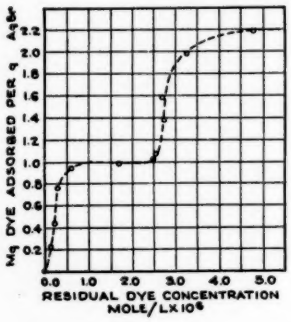


FIG. 3. Adsorption of dye VIIa to silver bromide; pH = 6.8; temp. = 25°C.

Experiments show that while the adsorption of these dyes to silver halide is very rapid in plain water, it is slowed down by the presence of gelatin, the rate of adsorption diminishing with the concentration of the gelatin.**

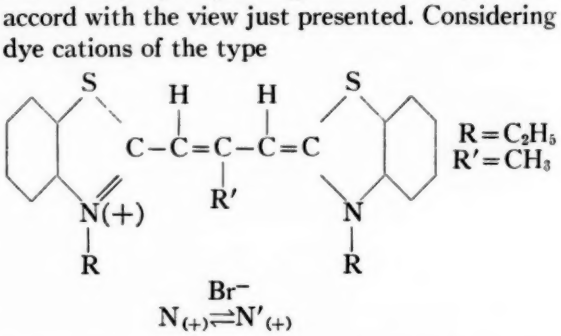
In consequence, according to the time allowed before measurement, the concentration of the gelatin, the temperature, a series of "apparent" adsorption isotherms may be obtained, as shown in Fig. 2. The retarding effect of gelatin can be ascribed to several factors—increased viscosity, lowering diffusion velocity, but still more the electrostatic attraction of dye cations (of the basic dye) for gelatin anions, or negatively charged gelatin (above the isoelectric point of the gelatin, i.e., pH 5), i.e., the silver halide has to compete with the gelatin. But, further, the dye has to compete with the gelatin which is also adsorbed to silver halide.[3] It is probably these last two factors which are the most important.

Although from water the adsorption is complete and irreversible there is some evidence for a slight resolution, i.e., equilibrium residual concentration, in gelatin. This may well be due, not so much to the electrostatic attraction as to the organic groups in gelatin having a solvent effect. This will be discussed in more detail in connection with the effect of *gelatin* on the absorption spectra of these dyes.

It appears probable that agreement of the "apparent" adsorption isotherms with a simple form of Langmuir's equation is coincidental and not of real significance. However, the plateaus in these curves appear to correspond to definite saturation levels. A primary level may be followed by a clearly marked secondary level, as shown in Fig. 3. The adsorption at the second level corresponds to the formation of a second monolayer, which is oriented in the opposite sense to the first, in that the organophile sides of the dye molecules face each other, while the ionizable and hydratable parts are presented to the water. This accounts for the repeptization of the coagulated AgBr hydrosol by the addition of further dye to the water beyond the point of coagulation.

ORIENTATION AND ADSORPTION DENSITY

It is only the first monolayer which is important for actual sensitizing, since as will be shown later in these studies, optimum sensitizing is effected well before the commencement of a second layer. The question now arises, as to how far the density of packing in the first layer is in accord with the view just presented. Considering dye cations of the type



it may be assumed that the atoms of the resonance chain (of conjugated double bonds) lie all in one plane, since only so could their valence shells be approximately regular tetrahedra in both extreme phases of the resonance.[8] This brings in one plane all of the atomic nuclei of the cation, except the H atoms of the R and R′ side groups, and one carbon of each C_2H_5. Preliminary rough calculations from known atomic radii and interatomic distances indicated that the

* Unpublished work.

** This affects much less the early stage of adsorption, which is chiefly important for sensitizing.

[8] To be published separately.

"edge-on" piling just discussed gave values of the right order of magnitude for the adsorption density. A more exact and detailed study was then made by M. L. Huggins of these Laboratories.[8] From data on atomic radii, bond distances and angles in analogous compounds, he has computed approximate areas occupied (in close packing) for dyes such as the above polymethine and also for erythrosin: (a) for molecules lying flat, (b) for molecules on edge, (c) for molecules on end.

The results were as shown in Table I. These values were obtained disregarding specific effects upon the packing of the dye molecules of the arrangement of ions in the crystal surface. In a surface covered by dye ions, the distance between, e.g., Br^- ions in silver bromide, may be assumed the same as in the undyed crystal (4.07A). The area per Br^- ion in an octahedral (1 : 1 : 1) face is then $(4.07)^2 \times \frac{3}{2} = 14.34A^2$. Huggins has calculated various possible unit cells in the surface layer, and therefrom the number of Br^- ions per dye ion either (a) in register with Br^- ion (for erythrosin dye F III, with Ag^+ ion layer, but equivalent) (b) close packed (Table II).

Values for other dyes were calculated similarly, and we may now compare the calculated results with our experimental results. These latter were obtained as follows: Adsorption measurements as described were run using a dilute silver bromide emulsion of medium to large grain size. The primary saturation level, or first plateau, was taken as corresponding to the adsorption density of a primary monolayer. We then require to know the surface area per gram of the silver halide. In the case of photographic emulsions, with crystallites running up to 4μ in diameter, this can be obtained by photomicrographic determinations of the size-frequency distribution, from which is obtained the total projected area as the integrated area-frequency curve. A correction can be made for the surface occupied by the sides, from measurements of the average thickness of the grains, which in the present case were relatively thin plates.

TABLE I. *Average area for close packing.*

ORIENTATION	DYE IIb	DYE FIII
(a) Flat	$140A^2$	$132A^2$
(b) Edge-on	$58A^2$	$78A^2$
(c) End-on	$26A^2$	$75A^2$

TABLE II. *Number of* Br^- *ions per dye ion.*

DYE	ORIENTATION	IN REGISTER WITH Br^- LAYER		CLOSE PACKED	
IIb	Flat	15	12	9.5	10
	Edge-on	4	5		4
	End-on	2	3	1.8	1.9
FIII	Flat	10	9	9.2	
	Edge-on	6		5.5	
	End-on	6		5.2	

TABLE III. *Limits calculated as in register or close-packed.*

DYE	EXPERIMENTAL: INCLUDING SIDES	EXPERIMENTAL: WITHOUT SIDES	*R*	END	EDGE	FLAT
Vc	6.44	3.87	4∼6	2.0∼3	4.0∼5	8.6∼15
VIIIb	7.37	4.43	4∼7	2.0∼3	3.8∼5	10.5∼15
Ia	7.27	4.36	4∼7	2.0∼3	4.7∼6	10.6∼15
IIb	5.02	3.02	3∼5	2.0∼3	4.0∼5	9.5∼15
IVb	6.00	3.60	4∼6	2.3∼3	4.0∼5	9.5∼15
VIIa	6.58	3.95	4∼6	2.0	4.0∼5	9.5∼15
FIII Erythrosin	13.5	8.10	8∼14	6	6	10

Results obtained in this way are collected in Table III. *R* gives rounded figures, for the bromide ion coverage, for with and without assumed sides of the crystals, the most probable value lying between. It will be seen that in the case of all the polymethine (cyanine) dyes, the experimental values agree with the vertical edge-on piling or orientation already suggested. The values for erythrosin approach more nearly to a flat orientation, but we believe that this requires further investigation, since from other considerations—chiefly optical and to be discussed under "The Mechanism of Optical Sensitization"—this dye also appears to be oriented in the edge-on position. Erythrosin differs from the cyanine dyes in that it is definitely *reversibly* adsorbed. Adsorption densities of sensitizing dyes have been discussed in previous publications. Sheppard and Crouch[1] found for Orthochrome T (Dye VIIIb) a value of 2.3 bromide ions per dye molecule adsorbed, value taken from the plateau part of the curve. This value appears to indicate a much greater

adsorption density than we have observed; the explanation has now been found in the fact that this dye shows a well marked two-stage adsorption, the plateau found by Sheppard and Crouch corresponding to a bimolecular layer. Hence, the value for the monolayer, 4.6 Br^- ions per mole-

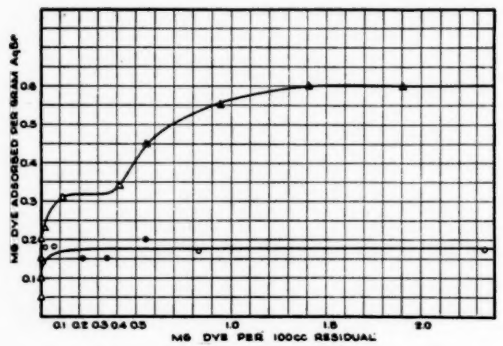
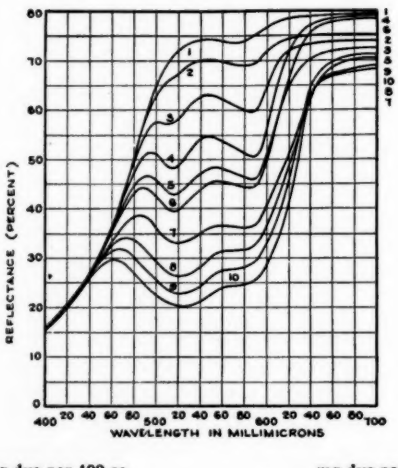


Fig. 4. Effect of dye concentration on amount of dye adsorbed for dye IIb for precipitated silver bromide; Δ dyed from water; o dyed from butyl alcohol.

cule, is in line. Considerably larger values—10 Br^- ions per dye molecule for carbocyanines and 20 Br^- ions for dicarbocyanines (dyes I, II and III) were reported by Leermakers, Carroll and Staud[5] from photographic sensitizing results, and indeed from the optimum sensitizing concentration. Their value for a monomolecular layer of dye IIb molecules lying flat in close packing on the surface was 150A², with which our value of 140A² is in good agreement. These values would indicate for saturation that the dye molecules were lying flat on the surface. However, we shall show later that optimum sensitizing is frequently reached at a coverage of the order of 50 percent of saturation (for some dyes less, for some more). Also, the slowness with which equilibrium is reached in the presence of gelatin might have made their results,* as also those of Bokinik, considerably lower than those now found. Finally, the packing-density and the orientation which our experiments lead to, appear to be much more consistent with other properties of the adsorbed dye layers. These are (a) the effect of adsorbed dye on the contact angle water: silver bromide. Experiments show that the adhesion tension of water is greatly lowered by the adsorbed dye layer, as would be the case with the organophile part of the molecule externally oriented, (b) the effect of adsorption on the absorption spectrum of the dye. While this will be discussed more fully in a later section, it may be said here that measurements of the absorption spectrum of the silver halides dyed with polymethine dyes show that, at any rate as the adsorption approaches saturation, part of the absorption spectrum corresponds not to that of the molecularly dispersed dye in solutions, but to a condensed form, such as is produced from aqueous solution by the addition of salt.[5] It has also been shown that under these conditions the sensitivity-spectrum corresponds with this. In view of this, and the nature of the photolysis (see subsequent paper), the conditions of edge-on, parallel piled orientation appears the only one satisfying all the facts.

A rough picture of the surface distribution of the dye molecules at high surface densities may be obtained by shaking elongated grains, e.g., of rice, in a single layer in a flat tray. At "saturation" it will be seen that there are many packets of parallel piled granules, with oddly ordered single, etc., grains between. The model is inadequate, because it takes no account either of the attractive forces between the dye molecules themselves, nor of any orienting effect of subjacent ions of the crystal lattice.



No.	mg dye per 100 cc Emulsion No. 1008	No.	mg dye per 100 cc Emulsion No. 1008
1	0.05	6	1.00
2	0.10	7	1.50
3	0.30	8	2.50
4	0.50	9	3.75
5	0.75	10	5.00

FIG. 5. Dye IVb. Reflection spectra of emulsions coated on plates with various concentrations of dye IVb.

* Cf. footnote (**) page 268.

Adsorption from Organic Solvents

The polymethine dyes are much more soluble in certain organic solvents, notably alcohols, than in water. It is customary to use methyl or ethyl alcohol in the preparation of concentrated stock solutions, and a certain amount of alcohol is usually present in sensitizing solutions when the dye is added to the emulsion. Hence, it is important to consider the effect of such an alcohol on adsorption and sensitizing. It has been found by Leermakers, Carroll and Staud[5] on the basis of comparison of the absorption and sensitivity spectra that adsorption is effected from alcoholic solution (methanol). From dilute dye solutions in aqueous gelatin they obtained a sensitivity spectrum markedly different from that of relatively more concentrated aqueous solutions (see Figs. 10 and 11 of their paper), and this they attributed to adsorption of the dye as discrete unaggregated molecules.

On repeating and extending their experiments we were unable to obtain any evidence for adsorption upon silver bromide grains from emulsions, of polymethine dyes, *viz.*, dyes IIb and IVb, from methanol solution, the latter being pure and as anhydrous as possible under the experimental conditions.

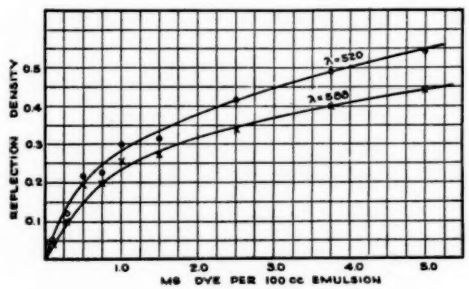


Fig. 6. Dye IVb, 1008 emulsion. The effect of dye added to an emulsion on the calculated reflection density of the two pronounced bands.

Summarizing the results of many experiments, it was found that both dyes IIb and IVb are definitely adsorbed to pure silver bromide precipitated in the absence of gelatin. A comparison of the adsorptions of dye IIb from butanol and from water on the same precipitated silver bromide is shown in Fig. 4. The adsorption from water occurs in two stages, the second level being

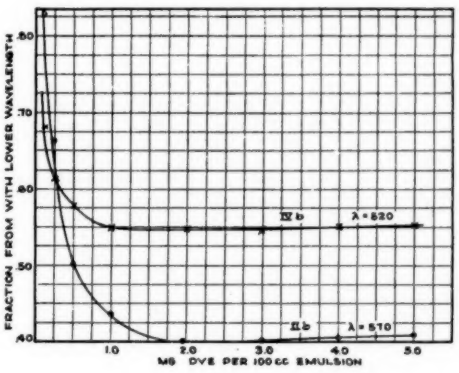


Fig. 7. Effect of concentration of dye added to an emulsion on fraction of dye present in form of lower wave-length band.

at twice the saturation for the first. Such double plateaus have been reported in unpublished work of Davey, of the Research Laboratory of Kodak Limited, Harrow, England, and also by ourselves, with other dyes, and an explanation has been given already. The adsorption from alcohol appears to be irreversible, since repeated extraction with methanol only removed minute amounts of retained dye, accountable by mechanical occlusion. It amounted to about 55 percent, at saturation, of the primary saturation level from water. Now spectral reflectance curves of silver bromide dyed with various concentrations in water of dyes IIb and IVb show the presence of *two* absorption bands (cf. Fig. 5), the relative intensities of which approach to a constant ratio as the degree of adsorption increases. This effect is shown in Fig. 6. These two bands correspond to the visibly pink form from alcohol (α-band at 570 mμ and supposed corresponding with the absorption at 540 mμ in alcohol solution) and to the purple-blue form as adsorbed to AgBr, but which is not observed in aqueous solution, except transiently on saturation with KBr. This absorption band, at 625 mμ with dye IIb, differs considerably from the β-band in water at 505 mμ. If the value $D_r = \log R0/R$ where R is the reflectance, be taken as a rough measure of the amount of dye adsorbed in the two forms from water, and plotted as a function of the concentration of dye added, we obtain the curves in Fig. 7. The proportion adsorbed at saturation for dye IIb is 40 percent, which is in

fair agreement with the 55 percent value for saturation from butanol.

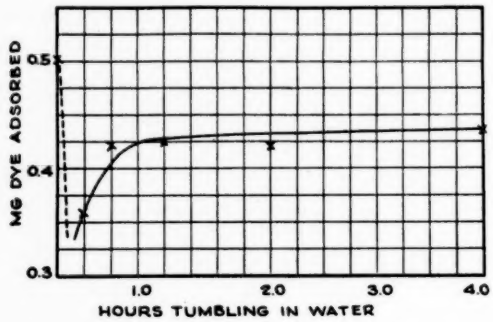


FIG. 8. Effect of time of treatment with alcohol of precipitated silver bromide dyed with dye IIb from water on amount of dye on grains.

The nature of the two forms of the dye on the silver halide is of considerable importance for the theory of optical sensitizing. An interesting observation on the dye adsorbed to pure silver bromide was reported by Leermakers, Carroll and Staud.[5] They observed that precipitated AgBr dyed pink from methanol turned bluish when wetted with water; conversely, when dyed bluish from water, dried, and wetted with alcohol, it turned pink. On investigating this more closely, we found that when the layer dyed from water is treated with alcohol, the dye is desorbed and goes into solution in the alcohol, from which it is resorbed in the pink form (cf. Fig. 8). On the other hand, when the pink layer is wetted with water, we found no evidence of desorption and solution but the change appeared to occur *in situ* on the surface. It is not evident at present what part water plays in the transformation. The dye does not give any spectral absorption in water corresponding to this form. Some observations on the effect of heating and drying the precipitate dyed bluish from water, whereby it turned pink, seemed to suggest that water molecules entered into the constitution of the bluish form, but this is not certain.

At present the tentative conclusion is that the pink form indicates a unimolecularly dispersed form of the dye, the form giving the band at 625 mμ a multimolecular aggregate.[5] The fact that the supposed unimolecular species gives a corresponding sensitizing band—as observed for other cyanine dyes[9,5]—is important. For, if single dye molecules can sensitize, the mechanism of quantum addition proposed by Scheibe[10] is unnecessary. A noteworthy fact is that while mere traces of gelatin on silver halide grains inhibit adsorption from alcohol, it only slows down adsorption from water, for both forms of the dye.

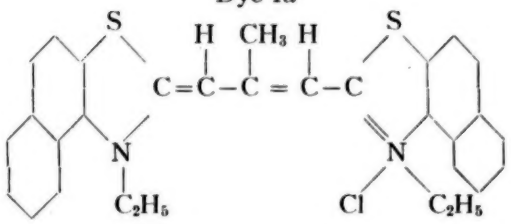
ADSORPTION AND ACTIVATION

For these dyes the data obtained do not indicate that there is any special adsorption to "activated" parts of the silver halide surface, such as is frequently postulated at present.[11] This appears from the fact that adsorption proceeds smoothly to saturation (primary level) and that this saturation corresponds to just the geometrically possible number of molecules standing closely packed on edge. Again, the spectral absorption is not changed from that given by the dye in solution, according to its aggregation state. Hence, there appears to be no significant adsorption energy of the dye to the silver halide lattice, over and above that existing as between dye cation, and a halide ion (in the case of the basic, polymethine dyes), or anion and a silver ion. The considerations advanced by J. H. de Boers, in his discussion of "The Absorption of Light by Matter in the Adsorbed State"[11] with regard to the effect of the adsorption energy on spectral absorption, do not appear to be pertinent in the case of optical sensitizing.

The dyes used in this work were prepared by L. G. S. Brooker, and their purity controlled by analysis. The numerical references—e.g., Ia, etc.—are used for brevity, and as far as possible coincide with the numbers of Leermakers, Carroll and Staud.[5] We have subjoined a letter, *a*, *b*, *c*, to indicate the anion, *a*=chloride, *b*=bromide, *c*=iodide. The actual formulae are as follows:

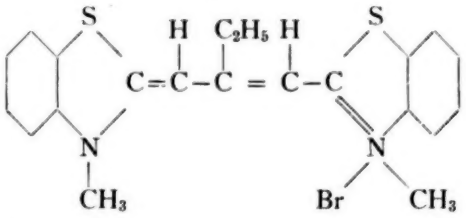
[9] S. E. Sheppard, Phot. J. **32**, 300 (1938).
[10] G. Scheibe, Naturwiss. **25**, 795 (1937).
[11] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, 1935), p. 180.

Dye Ia



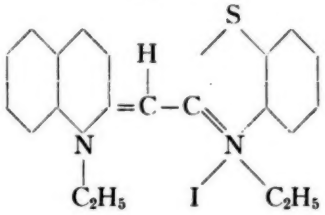
2 : 2′-diethyl-8-methyl-3 : 4–3′ : 4′-dibenzothiocarbocyanine chloride

Dye IIb



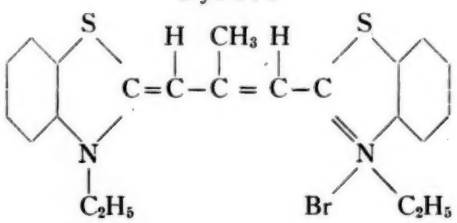
2 : 2′-dimethyl-8-ethylthiocarbocyanine bromide

Dye IIIc



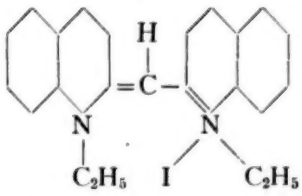
1′ : 2-diethylthiopseudocyanine iodide

Dye IVb



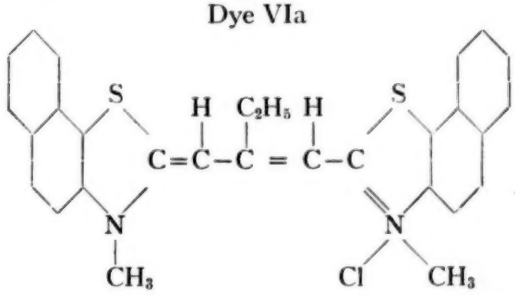
2 : 2′-diethyl-8-methylthiocarbocyanine bromide

Dye Vc



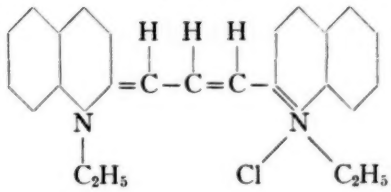
1 : 1′-diethylpseudocyanine iodide

Dye VIa



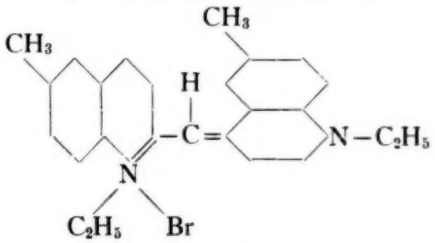
2 : 2′-dimethyl-8-ethyl-5 : 6–5′ : 6′-dibenzothiocarbocyanine chloride

Dye VIIa



1 : 1′-diethylcarbocyanine chloride

Dye VIIIb (orthochrome T)



1 : 1′-diethyl-6 : 6′-dimethylisocyanine bromide.

Absolute Values of the Velocity Constants in the Formation of Semiquinone*

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(Received February 4, 1939)

A mechanism for the autoxidation of hydroquinone and its homologs was presented in a previous paper. From this mechanism it is now possible to calculate a lower limit for the absolute velocity constant of the formation of semiquinone ions from quinone and doubly charged hydroquinone ions, and an estimate of this constant can be given in the analogous case of ψ-cumohydroquinone. In both cases, the velocity constant is found to be remarkably high; under special experimental conditions the velocity of this reaction should become of the same order of magnitude as the velocity of the recombination of the doubly charged hydroquinone ions with hydrogen ions, thus providing a test for this latter velocity.

THE catalytic action of ψ-cumoquinone in the autoxidation of ψ-cumohydroquinone reaches a saturation value with high ψ-cumoquinone concentrations. This was shown in a previous paper[1] to be caused by a reaction between the semiquinone and the ψ-cumoquinone which removes the former from the attack of the oxygen. Thus, the kinetics of the autoxidation are described, at low concentrations of the quinone, by the equation:

$$dx/dt=(k_1/2)(\text{cumohydroquinone}^{--})\cdot(\text{cumoquinone}) \quad (1)$$

and at high concentrations of the quinone, by the equation:

$$dx/dt=(k_1/2)(\text{cumohydroquinone}^{--})\cdot(k_2/k_3)(O_2). \quad (2)$$

The velocity constants k_1, k_2 and k_3 correspond to the formation of a semiquinone, to its oxidation and to its reaction with ψ-cumoquinone, respectively. It was further assumed that for the less substituted homologs of hydroquinone and for hydroquinone itself, the experiments give a course of the reaction which follows entirely Eq. (2). Eq. (2) is valid only in the region where the rate of reaction of the semiquinone with the quinone is high compared with the rate of oxidation of the semiquinone as follows:

$$k_3(\text{quinone})>k_2(O_2).$$

This condition seems to be fulfilled with hydroquinone and its lower homologs for even the smallest quinone concentrations which have been controlled experimentally.[2] It is with certainty valid onwards from a quinone concentration of 7×10^{-4} mole/liter.

With these premises, the absolute value for k_1 can be estimated in the case of ψ-cumohydroquinone and durohydroquinone,[3] and a lower limit of this value can be calculated in the case of hydroquinone. In all cases, it will be seen that the value for the constant k_1, giving the velocity of formation of the semiquinone, is remarkably high. Under special conditions, this reaction may even compete with ionic recombination.

For ψ-cumohydroquinone, according to Eq. (1), the experimental value for the reaction rate is:

$$\Delta x/\Delta t=k_1/2,\ (\text{cumohydroquinone}^{--})\cdot(\text{cumoquinone}).$$

The concentration of the double-charged ion is equal to

$$(\text{cumohydroquinone})K_1\cdot K_2\cdot(1/(H^{\cdot})^2),$$

where K_1 and K_2 are the first and second dissociation constant of ψ-cumohydroquinone. Therefore,

$$k_1=2\frac{\Delta x}{\Delta t}\cdot\frac{(H^{\cdot})^2}{(\text{cumohydroqu.})(\text{cumoqu.})}\cdot\frac{1}{K_1K_2}.$$

In this equation all the data are available from

* Communication No: 718 from the Kodak Research Laboratories.

[1] G. Kornfeld and A. Weissberger, Communication No. 702, J. Am. Chem. Soc. **61**, 360 (1939).

[2] T. H. James, J. M. Snell and A. Weissberger, J. Am. Chem. Soc. **60**, 2084 (1938).

[3] T. H. James and A. Weissberger, J. Am. Chem. Soc. **60**, 98 (1938).

the experimental evidence,[3] with the single exception of the dissociation constants K_1 and K_2. They are not known for ψ-cumohydroquinone, but have been determined by Sheppard[4] for hydroquinone: $K_1=1.75\times10^{-10}$ and $K_2=4\times10^{-12}$, at 25°C.

Since L. Michaelis[5] found a very similar value for toluhydroquinone, the constants, as a first approximation, will be assumed to have the same values for ψ-cumohydroquinone.

In this way the velocity constant of the semiquinone formation, from the average experimental results, is:

$$k_1=10^8 \text{ mole}^{-1} \text{ sec.}^{-1} \text{ liter}^1.$$

This means that if the reaction partners were present in molar concentration, they would be converted to semiquinone in 10^{-8} second. If every collision were successful, the time needed would be $10^{-11.4}$ second instead, since the reaction velocity of a bimolecular reaction, with all the collisions being effective, is given, at most, by the expression:

$$k'=10^{11.4} \text{ mole}^{-1} \text{ sec.}^{-1} \text{ liter}^1,$$

where 10^{-7} cm is assumed to be the molecular diameter. Out of about 3000 collisions, then, one is effective in the formation of a semiquinone. This efficiency is very high and corresponds to an activation energy of less than 5000 calories.

The number of collisions, however, was calculated on the basis of the assumption that the laws governing gas kinetics are applicable also to dilute solutions. On this point divergent views have been expressed. From theoretical reasons, Wynne-Jones and Eyring[6] as well as Evans and Polanyi[7] concluded that collisions should be a hundred times as frequent in solution as in the gas phase. But in a critical discussion on this point Moelwyn-Hughes[8] pointed out that all the available experimental evidence[9] confirms the quantitative agreement between kinetics in gases and solutions. The formerly mentioned assumption would yield an activation energy of more than 7000 calories which is still a remarkably low value.

But as already mentioned at the beginning, the dissociation constants for ψ-cumohydroquinone have not been determined, and the extrapolation from the values for hydroquinone may be wrong by one or two orders of ten. The same applies to durohydroquinone which, moreover, reacts more slowly than ψ-cumohydroquinone. In order to get information about a lower limit, at least, of the velocity constant for the formation of a semiquinone, the data for hydroquinone itself will now be evaluated.

It was mentioned at the beginning that, for this purpose, Eq. (2) can be used which with certainty is valid for quinone concentrations from 7×10^{-4} mole/liters upwards. This gives a minimum value for k_3/k_2, since, for that concentration, $k_3(\text{quinone})\geq10k_2(O_2)$. The concentration of oxygen can easily be determined from the pressure and the known solubility in alkaline solutions. In this way, from the experimental data it is found that for hydroquinone the velocity constant (for the semiquinone formation) is:

$$k_1\geq10^{6.4} \text{ mole}^{-1} \text{ sec.}^{-1} \text{ liter}^1.$$

Hence, at least one collision in about one hundred thousand collisions is successful; and the activation energy of the reaction is less than 7000 calories, at the utmost. If Moelwyn-Hughes is right in assuming that the kinetic laws for gases are valid for dilute solutions, then these limits are quite definite. They correspond, however, only to a lower limit of the velocity constant without any indication as to how far above the limit the real value will be found. There are other considerations, however, which can narrow down the possibilities.

The formation of the semiquinone results from the reaction of the doubly charged hydroquinone ion with the quinone. It is assumed that the ions are present in a concentration corresponding to the equilibrium of electrolytic dissociation. This assumption is generally justified, since the ionic recombination is supposed to occur at every collision, so that no other reaction is likely to compete with it. Experimental evidence shows

[4] S. E. Sheppard, Trans. Am. Electroch. Soc. **39**, 440 (1921).
[5] Private communication to Dr. A. Weissberger.
[6] W. F. K. Wynne-Jones and H. Eyring, J. Chem. Phys. **3**, 492 (1935).
[7] M. G. Evans and M. Polanyi, Trans. Faraday Soc. **31**, 875 (1935).
[8] E. A. Moelwyn-Hughes, Trans. Faraday Soc. **32**, 1729 (1936).
[9] E. A. Moelwyn-Hughes, Acta Physicochimica U.R.S.S. IV, 173 (1936).

that this assumption is justified in the present case, since the velocity is found to be proportional to the square of the hydroxyl-ion concentration, i.e., to the concentration of the doubly charged ions in their established equilibrium of dissociation. Therefore, an upper limit for the velocity of the semiquinone formation can be found, by postulating that this velocity shall be not more than one-tenth of the velocity required for the recombination of the doubly charged hydroquinone ion with a hydrogen ion.

If, tentatively, the former lower limit is taken to be identical with the upper limit, one collision in 10^{-5} will be successful in the formation of a semiquinone, at an approximate molar quinone concentration of 10^{-3}. With the hydrogen ion, every collision will be successful and it may be assumed that the number of collisions will be about ten times as large. With a *p*H of about 8, the two velocities will then have the ratio: $10^{-5}\times10^{-3}$ to 10×10^{-8}, which gives 1 to 10, the limiting condition for the existence of an established equilibrium of electrolytic dissociation and for the dependence of the velocity of the square of the hydroxyl-ion concentration.

This shows that, indeed, the lower limit cannot be supposed to be very much below the actual velocity constant. At the same time one can foresee that changed conditions—especially an increase in the quinone concentration—may change the dependence of the reaction velocity on the hydroxyl-ion concentration from the second power to a value lying between the first and second powers.

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

Vibrational Assignments in Ethane

In a recent number of this Journal, Crawford, Avery and Linnett[1] reported certain Raman and infra-red observations on ethane, and gave an excellent resumé of the available data and their interpretation. As this molecule has four different fundamental vibrations with frequencies approximating 1400 cm^{-1}, a unique correlation with observed bands is perhaps not yet possible. Some qualitative arguments may be presented, however, in favor of an interpretation slightly different from the one referred to.

Two nondegenerate parallel vibrations due to hydrogen bond deformations are found in ethylene at 1444 cm^{-1} and 1623 cm^{-1}, the former observed in the infra-red and the latter in Raman scattering. The motions differ primarily in phase, the lower frequency involving an oscillation of the two carbon atoms moving together, while at the higher frequency they move in opposite directions. Of the two corresponding vibrations in ethane, the antisymmetric one appears in the infra-red at 1380 cm^{-1}, and the symmetric oscillation has been assigned the frequency 1375 cm^{-1}. There are several reasons why this does not seem plausible: (1) a consideration of the motion and a comparison with the ethylene frequencies indicates that it should certainly be greater than 1380 cm^{-1}, (2) no Raman line has been observed at 1375 cm^{-1} although the harmonic of this frequency appears, and (3) a comparison[2] with methyl halide frequencies (ν_3) suggests that it is too small by at least 100 cm^{-1}.

There is a fairly strong Raman line due to ethane near 1460 cm^{-1}, but polarization measurements[1] indicate that it must be due to a degenerate vibration, in spite of the fact that usually such bands are very weak. The infra-red measurements of Levin and Meyer[3] place this band center at 1461 cm^{-1}, one half-space below the position of the strongest line. (The maximum of smaller intensity at 1492 cm^{-1} may be due to the difference band $2955-1461=1494$.) However, an examination of the microphotometer curve on the 1460 cm^{-1} Raman line seems to indicate a weak polarized component on the high frequency side and not distinctly separated from the broad depolarized band. Its position may be estimated as approximately 1480 cm^{-1}. Why the Raman line due to the degenerate motion should be strong, and that due to the nondegenerate one weak, is not easy to explain, but it would be still more difficult to understand a vanishingly small Raman intensity supposing the frequency to be 1375 cm^{-1}. On the other hand, there is one of the motions for which the fundamental is inactive both in Raman and in infra-red, with which the latter frequency may be associated.

The assignment here proposed for the frequencies of the hydrogen bond deformations, as compared with those in Table II of reference 1, using the symmetry symbols for the point group D_{3h}, is

A_1': 1480 instead of 1375,
A_2'': 1380 unchanged,
E': 1460 instead of 1480,
E'': 1375 instead of 1460.

E. F. BARKER

University of Michigan,
Ann Arbor, Michigan,
February 23, 1939.

[1] B. L. Crawford, W. H. Avery and J. W. Linnett, J. Chem. Phys. 6, 682 (1938).
[2] A. Adel and E. F. Barker, J. Chem. Phys. 2, 627 (1934).
[3] A. Levin and C. F. Meyer, J. Opt. Soc. Am. 16, 137 (1928).

The Coupling of Vibrations with Electronic Levels in Rare Earth Compounds*

Many of the features of the absorption spectra of rare earth compounds have been accounted for by attributing the lines to transitions between $(4f)^n$ electronic configurations of the cation.[1] These levels are split by the electric fields within the solid into multiplets[2] giving rise to a number of possible transitions. However, it is necessary to assume coupling of vibrations with the electronic levels to account for the large number of lines actually observed. However, in no case in the knowledge of the authors has a definite absorption frequency difference been identified as a vibration frequency. It is the purpose of the present preliminary account of an investigation of the absorption spectra of the acetylacetonates of praseodymium and neodymium to present evidence for a vibration frequency of approximately 82 cm^{-1} and 103 cm^{-1}, respectively, for the two compounds.

The acetylacetonate compounds were chosen for investigation for the following reasons: (1) The fact that this type of compound possesses a molecular lattice should simplify the modes of vibration which couple with electronic levels; (2) the field perturbing the central ion should be approximately of octahedral symmetry since the work of Astbury[3] indicates that the tervalent acetylacetonate molecule probably consists of a cation surrounded by six oxygens at the corners of a regular octahedron with the

chain of three carbons of the β-diketone molecule spanning between a pair of oxygens.

The absorption spectra of solid anhydrous and hydrated praseodymium and neodymium acetylacetonate were observed in the near infra-red and visible at temperatures of 78°K, 120°K, 193°K and 298°K. The spectrum of the anhydrous neodymium compound was similar to that of $NdCl_3 6H_2O$,[4] although it possessed fewer strong lines as was expected. That of the praseodymium compound was markedly simpler than the spectrum of $Pr_2(SO_4)_3 \cdot 8H_2O$.[5]

Plates taken at 120°K using appropriate absorption thicknesses and optimum exposure times showed progressions of very diffuse weak bands extending from strong absorption multiplets to shorter wave-lengths. These bands were separated by fairly constant intervals which averaged 82 cm^{-1} in the case of $Pr(C_5H_7O_2)_3$ and 103 cm^{-1} in the case of $Nd(C_5H_7O_2)_3$. It seems reasonable to interpret these separations as vibrational frequencies because of their appearance and the fact that a qualitative application of the Franck-Condon principle explains their intensity. It is interesting to note that the praseodymium compound is the less stable of the two, a fact which might correlate with its lower vibration frequency. One or two similar intervals could be found on the long wave side of nearly every multiplet. The accuracy of the measurements is approximately ± 2 cm^{-1}.

If a term scheme which is a combination of those proposed by Ellis[1] and Mukherji[1] is used, the Stark levels produced by splitting due to an octahedral field plus the vibration levels are adequate to account for the lines in each multiplet of the neodymium compound. A similar scheme applies partially in the case of $Pr(C_5H_7O_2)_3$. However, many assignments are not unique, hence it seems advisable to calculate the theoretical splitting of all the excited states using a field which produces the splitting observed for the ground state of the ion before putting forth a scheme of analysis.

A more detailed description of the experimental work and discussion of results will be presented later.

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New Jersey Zinc Company (of Pennsylvania),
Palmerton, Pennsylvania,
March 3, 1939.

* From work done by W. S. Herbert in partial fulfillment of the requirements for the Ph.D. degree at the Ohio State University.

[1] H. A. Bethe and F. H. Spedding, Phys. Rev. **52**, 454 (1937). Cf. references cited. H. Gobrecht, Ann. d. Physik **28**, 673 (1937); J. H. Van Vleck, J. Phys. Chem. **41**, 67 (1937); C. B. Ellis, Phys. Rev. **49**, 875 (1936); P. C. Mukherji, Ind. J. Phys. **11**, 123 (1937).
[2] H. A. Bethe, Ann. d. Physik **3**, 133 (1929).
[3] Astbury, Proc. Roy. Soc. **A112**, 448 (1926).
[4] F. H. Spedding and H. F. Hamlin, J. Chem. Phys. **5**, 429 (1937).
[5] Spedding, Howe and Keller, J. Chem. Phys. **5**, 416 (1937).

A Solution of an Equation Occurring in the Theory of Consecutive Reactions

The reactions

$$B+B \rightarrow D+\cdots \quad (k_1),$$
$$B+D \rightarrow C+\cdots \quad (k_2),$$

where k_1 and k_2 are the rate constants of the respective bimolecular reactions, lead to equations for the variations with time of $[B]$ and $[D]$ whose solution is not easy. The primary differential equations are:

$$\dot{B} = -2k_1B^2 - k_2BD,$$
$$\dot{D} = k_1B^2 - k_2BD,$$

where B and D represent the concentrations of the respective substances. Differentiating the first and substituting in the result the value of $\dot{D}$ from the second and D from the first, these reduce to

$$B\ddot{B} + B^2\dot{B}(2k_1+k_2) - \dot{B}^2 + 3k_1k_2B^4 = 0.$$

Let $2k_1+k_2=l$, $3k_1k_2=m^2$, $e^{\beta}=B$:

$$\ddot{\beta} + l e^{\beta}\dot{\beta} + m^2 e^{2\beta} = 0.$$

Expressing β as a power series in t, expanding $e^{\beta}\dot{\beta}$ and $e^{2\beta}$, and equating coefficients of like powers of t, one obtains:

$$\beta = \ln a + a_1 t - \tfrac{1}{2}a(la_1 + m^2 a)t^2 + \text{terms in higher powers.}$$

The constants of integration are a and a_1; the former is equal to the initial value of $B(B_0)$, and the latter equals $-2k_1B_0$. The error caused by neglecting powers of t higher than the square is equal to the quadratic term times atk_1 or atk_2 according as $k_1/k_2 \gtrless 1$. This gives for B:

$$B = B_0 \exp\left(-2k_1B_0t - \tfrac{1}{2}k_1B_0^2(k_2-4k_1)t^2\right)$$

which is seen to be the normal exponential decrease minus a quadratic correction due to the second reaction. The error in this value of B due to neglect of higher powers of t is, for values of t ordinarily met with in reaction rate measurements, smaller than 1 part in 10^4. In any case it may readily be calculated.

Substituting B in the original equations gives $D=f(t)$. But often k_2 is all that is desired and k_1 is known. For example, a rate of dimerization being known, a rate of trimerization is wanted, assuming a mechanism of successive reactions. For this it is necessary to know the values of B and D at $t=t_1$; call them B_1 and D_1. Then simplification of the expression for D gives

$$k_2 = 2k_1 \frac{B_0 - B_1 - 2k_1B_0^2t_1}{D_1 - k_1B_0^2t_1}.$$

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Mallinckrodt Laboratory,
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Cambridge, Massachusetts,
March 5, 1939.

Raman Effect of Fluorotrichloromethane

Six Raman lines have been observed for fluorotrichloromethane using our usual equipment.[1] The sample was distilled into a Raman tube in the low temperature apparatus already described.[2] It was held at a temperature of about 0°C during the exposures. Illumination was by means of eight concentric neon-mercury lamps. No filters were used. Results are shown in Table I.

Eastman Spectroscopic Plates Type I-J and Type I-G were employed. Best results were obtained with the former. There was no noticeable photochemical action during a 46-hour exposure.

The material was furnished by the E. I. duPont de Nemours & Company and was a plant product considered 99 percent pure or better. We wish to thank Dr. A. F.

TABLE I. *Fundamental frequencies of fluorotrichloromethane.*

Δ cm^{-1}	% MEAN DEVIATION	EXCITING LINES*	NO. OF READINGS	RELATIVE INTENSITIES
243.7	0.33	*a b c*	13	5
349.5	0.20	*a c*	12	5
397.5	0.20	*a c*	9	4
535.3	0.26	*a b c*	14	10
833.2	0.17	*a c*	6	2 (broad)
1067.2	0.40	*a c*	3	0 (broad)

* $a = 4046$; $b = 4077$; $c = 4358$.

Benning of the Jackson Laboratory for the loan of this substance. Further consideration of these results will appear in a later publication.

University of Minnesota,
Minneapolis, Minnesota,
January 31, 1939.

GEO. GLOCKLER
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[1] Phys. Rev. **54**, 970 (1938).
[2] Rev. Sci. Inst. **9**, 306 (1938).

Explosion Limits of the Hydrogen-Oxygen Mixture

Conditions for the thermal explosion of the mixture $2H_2+O_2$ are described in the pressure-temperature diagram by a complicated curve, first investigated by Thompson and Hinshelwood.[1] Explosion takes place on the "explosion peninsula" (Fig. 1 between "upper" and "lower" limit) or, in general, for any p-T combination on the *right* side of this curve. The reaction has a finite rate for combinations on the *left* side. Immediately above the "upper" explosion limit the rate drops to a very low value and increases with pressure towards another, called the "third," explosion limit. It has not been quantitatively investigated because of the violence of the explosion expected, which ought to be greater than the violence of the "upper" explosion taking place at pressures as low as 16 cm or lower.

For the purpose of certain spectroscopic investigations of free radicals, we search for the conditions under which the thermal hydrogen-oxygen reaction would proceed at a fast, but still finite, well-reproducible rate. Expecting an occasional explosion, we shielded the apparatus by gauze screens. We started from the recent results of Prettre,[2] who found that a KCl surface makes the reaction more reproducible than it is in a clean glass or quartz vessel. Most of our experiments, therefore, were performed in Pyrex or quartz vessels covered with a visible deposit of KCl. The explosion at high temperature and pressure proved to be less violent than the destructive explosion of the mixture $2H_2+O_2$ at room temperature, started by a spark, which doubtless is due to the higher density in the latter case. During several hundred experiments conducted at pressures between 47 and 77 cm and temperatures between 540 and 575°C not a single vessel was broken.

The quantitative investigation of the third explosion limit is complicated by an inhibition period. This has the effect that for a given temperature a certain pressure range will ultimately lead to an explosion; the higher the pressure, the shorter the inhibition period. We define the explosion limit as the p-T combination for which the inhibition period vanishes. Each value of the third explosion limit, therefore, was obtained from a considerable number of explosions in which the inhibition period was measured against the pressure for a given temperature. The resulting curve of the third explosion limit in a vessel with a KCl surface is given in Fig. 1*D*. The same figure gives the "upper" explosion limit *C* as it is modified by covering the surface with KCl; (as the rate of manipulation considerably affects this curve we repeated conditions as well as we could).

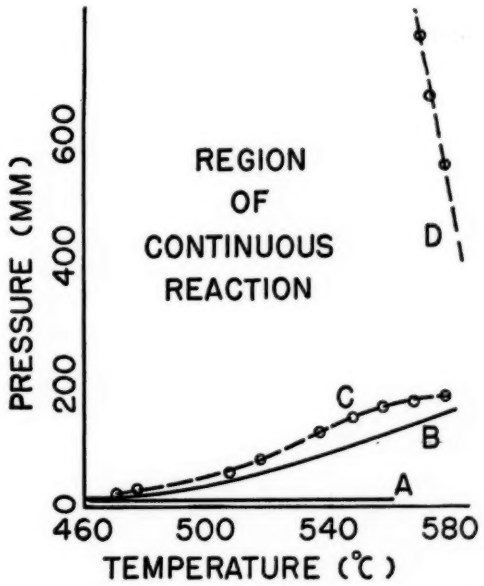

FIG. 1. Explosion limits of the mixture $2H_2+O_2$. *A*, lower limit; *B*, upper limit (both for clean glass or quartz); *C*, upper limit; *D*, third limit (both for KCl surface).

Only a few experiments were performed in a clean Pyrex vessel without KCl; the third explosion limit was reached at a far lower temperature than with a KCl surface. In a vessel of large diameter the third explosion limit came at lower pressures than in one with a small diameter—thus extending the area of explosion. This indicates that the walls somehow hinder the explosion.

The theory of Lewis and von Elbe[3] gives an approximate account of the third explosion limit, the first measurements of which are reported above. The theory correctly states that with increasing temperature the ignition takes place at lower pressure. Furthermore, it correctly predicts the effect of an increase in the diameter of the vessel.

While thus far the theory of Lewis and von Elbe seems successful, we do find difficulty in reconciling it with some other observations.

A more detailed account will be published at a later date.

Research Laboratory of Physics,
Harvard University,
Cambridge, Massachusetts,
March 15, 1939.

O. OLDENBERG
H. S. SOMMERS, JR.

[1] H. W. Thompson and C. N. Hinshelwood, Proc. Roy. Soc. **A122**, 610 (1929).
[2] M. Prettre, J. de Chimie Physique **33**, 189 (1936) and *Reactions en Chaînes* (Hermann et Cie, Paris, 1936).
[3] B. Lewis and G. von Elbe, *Combustions, Flames and Explosions of Gases* (Cambridge University Press, 1938).